U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-268 239

Factors Affecting the Collection Efficiency of Atmospheric Sulfate

Battelle Columbus Labs, Ohio

Prepared for

Environmental Sciences Research Lab, Research Triangle Park, N C

May 77

PB 268 230

EPA-600/2-77-078
May 1977

Environmental Protection Technology Series

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/2-77-076
May 1977

FACTORS AFFECTING THE COLLECTION EFFICIENCY OF ATMOSPHERIC SULFATE

by

R.W. Coutant

BATTELLE
Columbus Laboratories
Columbus, Ohio 43201

Contract No. 68-02-1784

Project Officer

Eva Wittgenstein
Sampling and Analysis Methods Branch
Atmospheric Chemistry and Physics Division
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-77-076	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE: FACTORS AFFECTING THE COLLECTION EFFICIENCY OF ATMOSPHERIC SULFATE		5. REPORT DATE May 1977
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): Coutant, R. W.		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Battelle Columbus Laboratories, Columbus, Ohio 43201		10. PROGRAM ELEMENT NO. 1AB712 BE-08 (FY-77)
		11. CONTRACT/GRANT NO. 68-02-1784
12. SPONSORING AGENCY NAME AND ADDRESS: Environmental Sciences Research Laboratory - RTP, N. C., Office of Research and Development, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED Final, 6/75 - 11/76
		14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

Factors that influence the collection and measurement of atmospheric sulfate were investigated. Special emphasis was given to those factors that cause the formation of extraneous sulfate during the sampling process. The factors considered were filter type and composition, ambient SO_2 concentration, temperature, relative humidity, ambient gas composition, sampling time and rate, storage time and conditions, and the presence of potential oxidation catalysts in the particular catch.

The approach of the investigation was twofold. After conducting an extensive laboratory program to identify and quantify significant sulfate generating interactions, a brief field study was performed to test the significance of the laboratory observations under typical field operating conditions.

The results of this investigation indicated that the most significant cause of sulfate sampling error is the interaction of basic filter components with ambient SO_2. This interaction is affected by ambient atmospheric conditions. A relationship based on established chemistry was developed for the prediction of sulfate error caused by this interaction. Recommendations of filter media appropriate for ambient sulfate monitoring and further development of a methodology are included.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution *Filter materials *Sulfates *Interactions Particles *Sampling *Efficiency *Sulfur dioxide		13B 07B 14B 13K

18. DISTRIBUTION STATEMENT: RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 99
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE A05 PC A01

EPA Form 2220-1 (9-73)

ABSTRACT

Factors that influence the collection and measurement of atmospheric sulfate were investigated. Special emphasis was given to those factors that cause the formation of extraneous sulfate during the sampling process. The factors considered were filter type and composition, ambient SO_2 concentration, temperature, relative humidity, ambient gas composition, sampling time and rate, storage time and conditions, and the presence of potential oxidation catalysts in the particulate catch.

The approach of the investigation was twofold. After conducting an extensive laboratory program to identify and quantify significant sulfate generating interactions, a brief field study was performed to test the significance of the laboratory observations under typical field operating conditions.

The results of this investigation indicated that the most significant cause of sulfate sampling error is the interaction of basic filter components with ambient SO_2. This interaction is affected by ambient atmospheric conditions. A relationship based on established chemistry was developed for the prediction of sulfate error caused by this interaction. Recommendations of filter media appropriate for ambient sulfate monitoring and further development of a methodology are included.

This report was submitted in fulfillment of Contract No. 68-02-1784 by Battelle's Columbus Laboratories under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period April 15, 1975 to November 30, 1976, and work was completed as of November 30, 1976.

CONTENTS

Abstract iii
Figures vi
Tables vii

1. Introduction 1
   Objective and General Approach 2

2. Laboratory Studies 3
   Apparatus 3
   Results 6
      Filter Composition 6
      Comparative Filter Responses 9
      Storage Effects 9
      Catalyst Effects 12
      Sampling Velocity 15
      Sampling Time 15
      SO_2 Absorption 16
   Discussion 20
      General Observations 20
      Oxidation Catalysts 20
      Chemistry of SO_2 Sorption by Filters 21
      Oxidation of Absorbed SO_2 27
      Sulfate Sampling Error 27
   Conclusions 30

3. Field Sampling Program 31
   Objective 31
   Approach 31
      Siting 31
         Fire Station No. 5 32
         Pymatuning State Park 32
         Columbus 32
      Experimental Plan 34
      Problem Areas 35
      Analyses 35
   Results 36
   Discussion 36
   Conclusions 42

4. Recommendations 44

References 46
Appendices

A. Gas Composition Data 48
B. Field Sampling Data 58
C. Los Angeles Field Sampling Data 85
D. Filter Identifications 90

Preceding page blank

FIGURES

Number		Page
1	Laboratory Sampling Rig.	4
2	Laboratory Instrumentation	6
3	Typical SO_2 Response Curve	17
4	Effect of Filter and Atmospheric Variables on SO_2 Sorption	26
5	Sulfate Error for Basic Filters.	29
6	Youngstown Field Sampling Area	33
7	Correlation Between Calculated and Measured Sulfur Differences.	37

TABLES

Number		Page
1	Filter Analyses (OES)	8
2	Filter Alkalinities	9
3	Filter Response Comparison	10
4	Effect of Storage on Apparent Sulfate	11
5	Particulate Composition - Run 4A	13
6	Catalyst Effect on Sulfate Collection	14
7	Results of Velocity Effect Experiment	15
8	Sampling Time Effects	16
9	SO_2 Sorption by Various Filters	18
10	Sorption of SO_2 by Basic Filters	19
11	Experimental and Predicted Excess Sulfates	28
12	Field Sample Summary	38
13	Field Sample Data	40
14	Statistical Comparison of ADL Filter Performance With Other Filters	41
A-1-A-9	Gas Composition Data	48-57
B-1	Elemental Analysis of Field Samples, Weight Percent	59
B-2-B-25	Field Atmospheric Conditions	60-84
C-1	Los Angeles Sampling Data	86
C-2-C-6	Los Angeles Ambient Conditions (Hourly Averages)	87-89
D-1	Filter Identifications	90

SECTION 1

INTRODUCTION

The need for accurate determination of ambient sulfate levels has been intensified in recent years because of the identification of sulfates as significant health hazards. While progress has been made in reducing atmospheric levels of sulfur dioxide, corresponding reduction in ambient sulfate levels has not, in general, been well correlated with the reductions in sulfur dioxide[1]. This fact along with both direct and indirect criticisms of the standard hi-vol sampling techniques for ambient sulfate collection have made obvious the need for a thorough investigation of sulfate sampling and analysis procedures.

Investigations such as those conducted by Lee and Wagman[2] and more recently by Radian personnel[3] and workers at Ford[4] have shown that filters commonly used for sulfate sampling can absorb SO_2 at ambient levels, and that this can lead to generation of extraneous sulfate during the sampling process. It can be inferred from other investigations[5] that the presence of potential SO_2 oxidation catalysts in ambient aerosols also may affect ambient sulfate measurements. Still other questions have been raised concerning the mechanical and dynamical factors involved in hi-vol sampling.

These potential sources of error during ambient sulfate sampling have been recognized by the U.S. Environmental Protection Agency, with the result that this program was developed as a part of EPA's overall efforts towards refinement of ambient air sampling and analysis methodology. The main thrust of this program has been examination of the effects of sampling and environmental factors on the formation of artifact sulfate. The present work included consideration of the effects of (1) filter type and composition, (2) ambient SO_2 concentration, (3) temperature, (4) relative humidity, (5) ambient gas composition, (6) sampling time and velocity, (7) sample storage time and conditions, and (8) particulate composition (SO_2 oxidation catalysts) on the formation of extraneous sulfate, in order to provide a quantitative base for the assessment of sulfate sampling methodology.

OBJECTIVE AND GENERAL APPROACH

The objective of this program was a thorough investigation of the factors that influence the collection and measurements of atmospheric sulfate. Special emphasis was given to those factors giving rise to extraneous sulfate formation as a consequence of sampling and measurement procedures.

The approach of this program has been twofold. The initial phase of the program was devoted to study of various sulfate collection parameters in the laboratory. Although this phase of the program involved controls possible only within the laboratory setting, ambient air served as a base for all measurements. The second part of the program involved a field sampling study in an attempt to verify the observations of the laboratory study under field operations conditions.

SECTION 2

LABORATORY STUDIES

APPARATUS

Ambient air was used as a base for all of the laboratory experiments. This was drawn into the laboratory at about 520 cfm through a stainless steel duct from a point some 50 feet above the building (ca. 50 ft about ground level). In the laboratory, the air stream was divided through two parallel stainless ducts (see Figures 1 and 2). At the top of each inside duct, injection ports and mixing orifices were added to enable spiking of the ambient air with various gases as needed for specific experiments. Sampling nozzles were fitted near the bottom of the parallel ducts, with provision for four identical sampling points in each duct. This arrangement permitted simultaneous isokinetic collection of as many as eight filter samples in any given run. Sample volume for each filter was about 1.2 percent of the total air flow. Standard 142-mm Millipore filter holders were fitted with modified conical inlets to achieve uniform distribution of particles over the filter surface. Outlets from the filter holders were fitted with calibrated orifices, and pumping across the orifices was achieved via a vacuum manifold using a Stokes Microvac pump with a capacity of 80 cfm. Normal 24-hour sampling volumes were of the order 1 m^3/cm^2.

Routine measurements were made of the SO_2 concentration (by flame photometry), NO_x (by chemiluminescence), the ozone concentration (by chemiluminescence), temperature, relative humidity, filter pressure drops, wind speed, and wind direction. Analyses for other gaseous components such as H_2S and NH_3 were made for specific experiments. Monitoring during the course of a run was automatic, with both strip-chart readouts and paper tape accumulation for computer analysis.

PROCEDURES

The laboratory apparatus was used for basically two types of experiments; 24-hour sampling runs, and shorter term examination of SO_2 sorption by filter media and by filters preloaded with various potentially active SO_2 oxidation

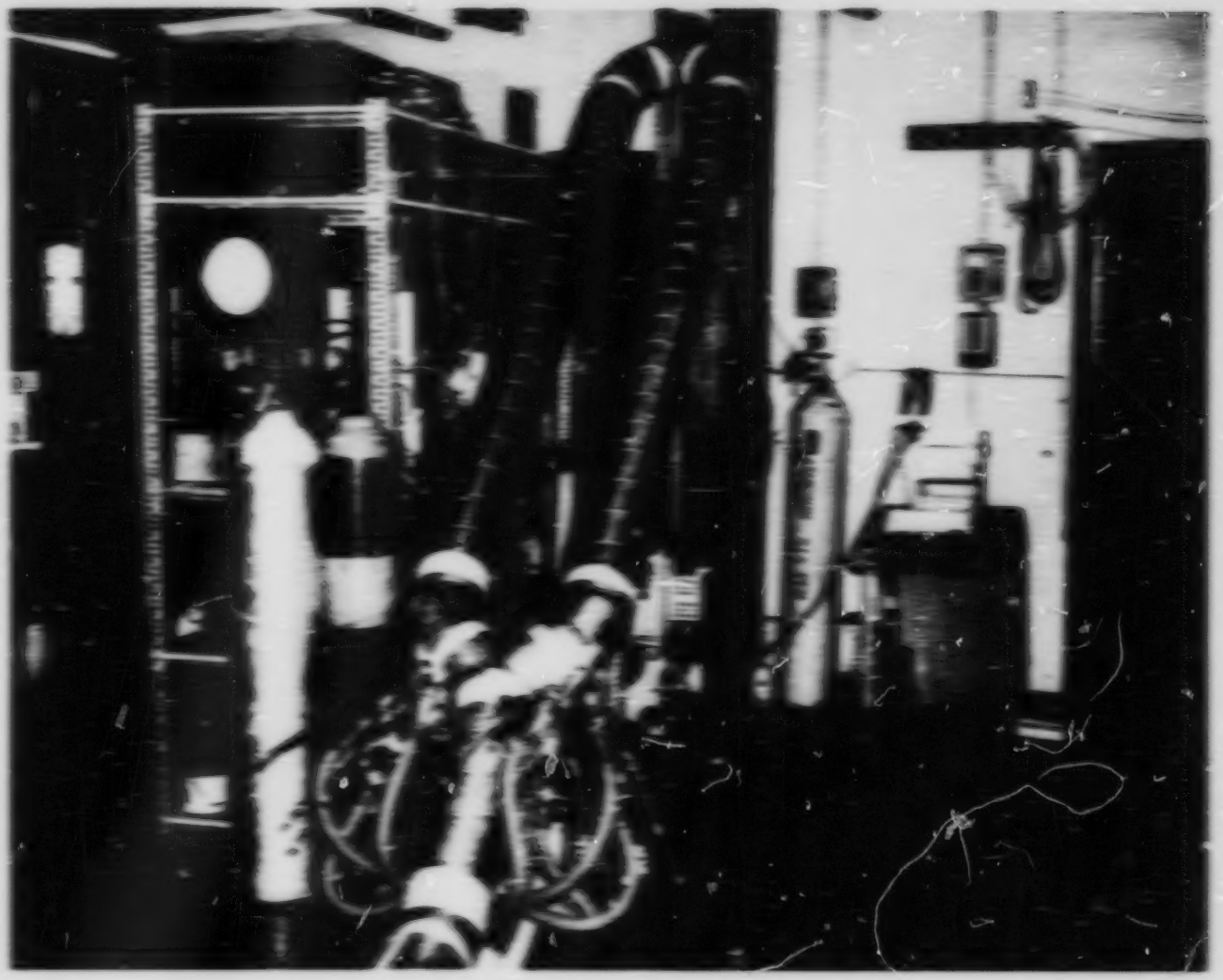

FIGURE 1. LABORATORY SAMPLING RIG

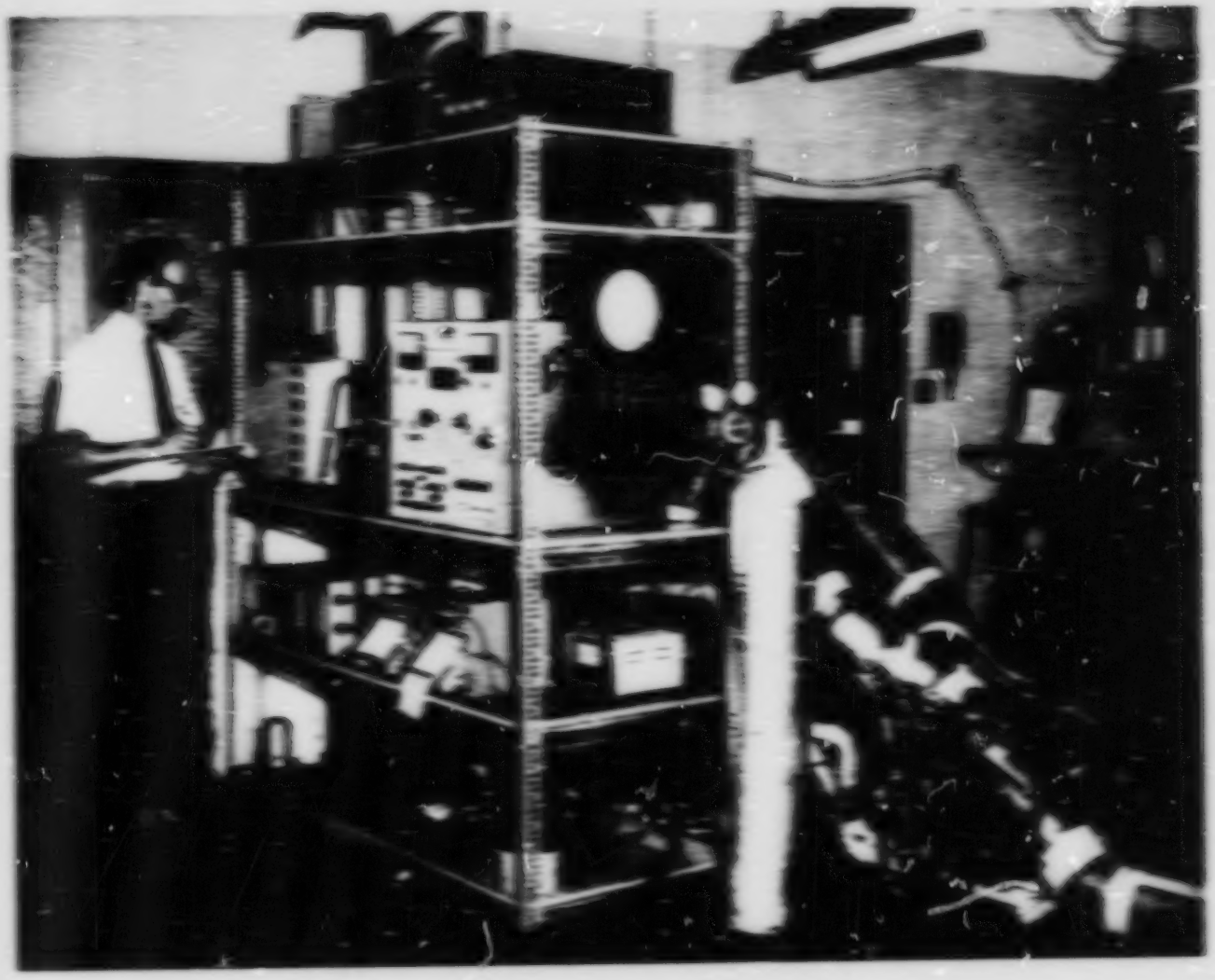

FIGURE 2. LABORATORY INSTRUMENTATION

catalysts. In the 24-hour runs, preweighed filters were mounted in the holders and were exposed to ambient air for a period of 24 hours. The filters were then removed, weighed in a constant temperature/humidity room, cut in half, reweighed, and submitted for analysis. In most cases, one half of each filter was analyzed as quickly as possible, and the other half was stored for possible analysis at a later date. Variations between samples collected in similar filters at the eight different sampling ports were random and were usually 1-3 percent based on either the total masses or on the sulfate catches.

In shorter term SO_2 sorption runs, the air flow in one branch of the parallel duct system was spiked with SO_2 to some appropriate level between ambient and 300 ppb. This level was preset without a filter in place. The filter was then placed in the system; the SO_2 was turned on; and SO_2 concentrations before and after the filter were monitored as a function of time. Inasmuch as fluctuations in ambient temperature, relative humidity, and SO_2 concentration were prone to occur during these experiments, data displaying variations greater than 2 percent in any one variable were rejected.

In examination of potential catalyst effects, dispersions of the agents in alcohol were sprayed onto the filters. In most cases, reagent grade or pigment grade agents were used. However, the vanadium oxide employed was a prepared sample (<17μ) of fly ash from an oil-fired power plant, and one of the iron oxide samples was a fly ash sample from a basic oxygen furnace.

Filter compositions were determined by standard optical emission spectroscopy (OES) techniques. Alkalinities and pH's for the filters were determined by ASTM D 202 procedures. Sulfate analyses for the laboratory program were performed primarily by the barium perchlorate/thorin titration method. However, near the end of the laboratory phase of the program, a Dionex ion chromatograph was obtained and was used for selected sulfate measurements.

RESULTS

Results of the different types of experiments are discussed separately below. Gas composition data for various run numbers cited in these discussions are tabulated in Appendix A.

Filter Composition

A complete listing of filters with identification of manufacturers is given in Appendix B.

Listings of OES results for the various filter types studied are shown in Table 1. Alkalinities and pH's for these same filter types are shown in Table 2. It is notable in these results that the glass fiber filters display high concentrations of sodium, potassium, calcium, and other basic components, and also show relatively high alkalinities and pH's. The high purity silica filters display only slightly basic character, and the cellulose acetate (Celotate) and Pallflex E 70/2075 W filters are slightly acidic. Samples of the Gelman AE filters showed a slight variation in alkalinity with examples from different positions in the package; a filter from the top of the package displayed the lowest alkalinity. While a hot-leach procedure (ASTM D 202) was used with most of the filters, one filter was leached at room temperature with the result of exhibiting only about half as much available alkalinity as the hot-leach samples.

Comparative Filter Responses

Three series of 24-hour sampling runs were made to evaluate differences between the responses of different filter media. Results of these measurements are shown in Table 3. While the absolute quantities of sulfate collected varied considerably, like pairs of filters consistently yielded similar results. Sulfate variations were therefore primarily due to differences between the filter media.

Storage Effects

Data given in Table 4 are the results of an experiment designed to reveal the effects of storage environment on apparent sulfate collection. In this experiment, two filters of each of four different types were exposed to identical ambient sampling conditions for a 24-hour period. Halves of the filters were then treated as follows:

(a) No storage - immediate analysis
(b) Storage for 4 weeks in dry air
(c) Storage for 4 weeks in wet air
(d) Storage for 4 weeks in argon.

Results of the sulfate analysis shown in Table 4 indicate large differences between apparent sulfate collections by the various filter types. An analysis of variance of this data reveals no significant variation with respect to storage condition, but differences between the responses of different filter types are significant at the 95 percent confidence level.

TABLE 1. FILTER ANALYSES (OES)

Element	Elemental Content, weight percent								
	MSA-1105DH	Gelman AE	Gelman AA	Spectro-grade	ADL	Millex	Calcitate	OAST	E 70/2075W
Al	3	3	0.4	3	0.1	1	0.0007	0.02	0.07
B	1	1	1	1	0.007	<0.001	0.0007	<0.002	1
Ba	0.01	0.2		0.1	<0.002	0.025	<0.0002		
Ca	0	0	1-2	0	0	0.03	0.003	0.02	0.5
Cd	<0.01	<0.01		<0.01	<0.01	<0.01	<0.0002		
Co	<0.001	<0.001		<0.001	<0.001	<0.001	<0.00007		
Cr	<0.002	<0.002	0.002	<0.002	<0.002	0.003	0.003	<0.002	0.002
Cu	<0.001	<0.001		<0.001	<0.001	<0.001	0.001		
Fe	0.04	0.04	0.1	0.04	0.02	0.05	0.0007	0.02	0.02
K	1	1	0.5	1	<0.02	0.8	0.01	0.01	0.4
Mg	2	2	1	2	0.01	0.02	0.002	0.01	0.2
Mn			<0.002					0.002	<0.002
Na	10	10	2-3	10	0.1	0.3	0.002	0.1	4-7
Ni	<0.001	<0.001	<0.001	<0.031	<0.001	0.002	<0.00007	0.001	<0.001
Pb			<0.002					<0.002	0.002
Sr	0.002	0.01	0.009	0.003	<0.002	0.002	<0.0002	<0.005	0.05
Ti	0.003	0.005	0.005	0.005	0.01	0.03	0.00007	0.003	0.003
V	<0.001	<0.001		<0.001	<0.001	0.002	<0.00007		
Zn	<0.01	0.1	<0.01	<0.01	<0.01	<0.01	0.001	<0.01	0.1
Zr	0.005	0.01		0.01	0.003	<0.001	0.00007		

TABLE 2. FILTER ALKALINITIES

Filter Type	pH	Alkalinity, meq/g
MSA-1106BH	9.2	3.1×10^{-2}
AOL Quartz	9.1	1.0×10^{-4}
Mitex	7.0	0.0
Spectrograde	7.2	1.0×10^{-4}
Celotate	6.65	(1.8×10^{-3})(a)
Pallflex QAST	8.1	3.8×10^{-3}
Pallflex E 70/2075W	6.2	(7.6×10^{-3})(a)
Gelman A	--	1.32×10^{-2}
Gelman AA	8.9	3.24×10^{-2}
Gelman AE(b)	9.4	4.0×10^{-2}
Gelman AE(c,d)	9.2	5.0×10^{-2}
Gelman AE(c,d)	9.3	4.89×10^{-2}
Gelman AE(c,d)	9.3	4.90×10^{-2}
Gelman AE(c,d)	9.2	4.34×10^{-2}
Gelman AE(c,e)	9.4	2.24×10^{-2}

(a) Acidic.
(b) Batch A.
(c) Batch B.
(d) Different positions in same package.
(e) Five-minute room temperature leach.

TABLE 3. FILTER RESPONSE COMPARISON

Run No.	Filter	SO_2, ppb	Apparent Sulfate, $\mu g/m^3$
1A1	Millex	180	29.8
1A2	Millex	180	31.8
1A3	Spectrograde	180	(33.5)[a]
1A4	Spectrograde	180	(32.1)[a]
1A5	Gelman AE	180	46.8
1A6	Gelman AE	180	46.3
1A7	Gelotate	180	26.6
1A8	Gelotate	180	24.4
2A1	Millex	225	11.9
2A2	Millex	225	11.6
2A3	MSA 11068H	225	25.2
2A4	MSA 11068H	225	24.9
2A5	ADL-Quartz	225	12.9
2A6	ADL-Quartz	225	12.7
2A7	Spectrograde	225	16.6
2A8	Spectrograde	225	-- [b]
1081	Pallflex E 70/2075-W	107	2.2
1082	Pallflex E 70/2075-W	107	6.0
1083	Gelman AA	107	24.0
1084	Gelman AA	107	26.0
1085	Pallflex QAST	107	14.4
1086	Pallflex QAST	107	11.0
1087	Gelman AE	107	28.1
1088	ADL	107	11.0

Average deviations: (sulfate/flow values)
Between filter pairs - 2.45
Between filter types - Run 1 - 10.75
Run 2 - 15.41
Run 10 - 39%

[a] Torn filter.
[b] Sample lost.

TABLE 4. EFFECT OF STORAGE ON APPARENT SULFATE

Filter Type	Storage Condition	Sulfate, $\mu g/m^3$
ADL	none	6.30
ADL	argon	(6.00)[a]
ADL	dry air	8.24
ADL	wet air	6.85
Celotate	none	14.17[b]
Celotate	argon	5.32
Celotate	dry air	9.89[b]
Celotate	wet air	8.16
Gelman AE	none	16.88
Gelman AE	argon	16.69
Gelman AE	dry air	17.19
Gelman AE	wet air	17.66
MSA 1106BH	none	12.55
MSA 1106BH	argon	15.49
MSA 1106BH	dry air	15.88
MSA 1106BH	wet air	14.32

(a) Sample lost, value estimated by Yates' Method [Kirk, Roger E., "Experimental Design: Procedures for the Behavioral Sciences", Brooks/Cole Publishing Co., Belmont, California, p 146-147 (1968)].

(b) Questionable data

Catalyst Effects

Table 5 shows the results obtained for the analysis of a typical particulate sample obtained in the laboratory sampling rig. The principal component of this ambient particulate sample is carbon; of those elements likely to exhibit activity as SO_2 oxidation catalysts, iron and manganese are the principal components. Both the ADL microquartz filters and the MSA 1106-BH filters were used. Analyses for sulfate, sulfite, and total nitrogen were carried out on both types of filters. The results reflect the differences in basicities of these two filter types; the more basic MSA filter shows higher sulfate and sulfite contents and lower nitrogen content. The oxygen content of the sample was estimated by requiring that the sample be electrically neutral, assuming that the carbon is present as elemental carbon. The deficit in negative species indicated by this procedure could, of course, also be logically represented in terms of carbonate. If the latter hypothesis is applied, the total mass balance is 119 percent rather than the 102 percent shown in Table 5. Either way, the mass balance seems reasonable in light of the number of individual analyses included in the summation.

A series of experiments was conducted to determine the possible significance of the presence of potentially active oxidation catalysts on the overall collection of ambient sulfate. These experiments included both short-term measurements of SO_2 absorption by filters that were preloaded with catalysts, and 24-hour sampling runs. Potential catalysts included Fe_2O_3 (from three sources including a basic oxygen furnace fly ash), MnO_2, carbon (acetylene black), vanadium oxide (high vanadium fly ash), ferric sulfate, manganese sulfate, and a mixture of carbon, and the oxides of iron, vanadium, and manganese. None of these materials was found to increase the level of SO_2 absorption exhibited by the filter. In fact, the more acidic iron and manganese sulfate-loaded filters tended to display less SO_2 absorption than the blank filters. An analysis of variance for the 24-hour sampling runs (Table 6) showed no significant effect (at the 90 percent confidence level) due to the presence of the oxides or carbon. Even with the vanadium fly ash sample, where the sulfate level appears to be relatively high, the result is not statistically different from the other samples.

TABLE 5. PARTICULATE COMPOSITION
RUN 4A

Species	Mass, mg	Particulate Composition, weight %
Total Mass	8.717	
Fe	0.25	2.87
B	0.00	0.00
Mg	0.13	1.49
Mn	0.03	0.34
Pb	0.13	1.49
Al	0.00	0.00
Na	1.25	14.34
Ti	0.00	0.00
K	0.13	0.49
Ca	0.00	0.00
Zr	0.00	0.00
$SO_4^=$	2.05 (3.24)[a]	23.52
$SO_3^=$	N.D. (0.11)[a]	--
$S^=$	N.D. (N.D.)[a]	--
Organic S	[illegible]	--
C	3.8	43.59
NH_4^+	0.48	5.51
NO_3^-	0.14	1.61
NO_2^-	<0.01	--
N	0.53 (0.35)[a]	6.08
O[b]	0.54	6.19
	Total	102.4

(a) MSA filter; all other data on ADL filter.

(b) By charge balance.

TABLE 6. CATALYST EFFECT ON SULFATE COLLECTION

Additive		Loading, mg	Sulfate, $\mu g/m^3$
Blank		--	7.36
Blank		--	8.28
Fe_2O_3		0.9	7.08
Fe_2O_3		2.8	7.07
MnO_2		2.85	11.09
C		2.1	7.30
C		6.4	8.23
Blank		--	19.6
Blank		--	19.3
MnO_2		0.35	20.5
MnO_2		1.95	13.9
MnO_2		3.80	22.3
BOF		1.46	19.6
V-ash		2.35	24.96
C	Mixture	1.84	21.5
BOF		0.5	
V-ash		0.5	
MnO_2		0.5	

Sampling Velocity

In this series of experiments, the flow rates in the two branches of the laboratory duct system were modified such that flow through one branch was approximately three times that in the other branch. Rate-controlling orifices in the filter holders were modified accordingly to provide approximately isokinetic sampling in each branch, and a 24-hour sampling run was conducted. Results of this experiment are shown in Table 7.

TABLE 7. RESULTS OF VELOCITY EFFECT EXPERIMENT

Filter Number(a)	Total Gas Volume, m^3	$\mu g\ SO_4/m^3$
1	56	3.90
2	142	6.44
3	54	6.00
4	150	3.48
5	54	3.76
6	143	3.38
7	56	2.77
8	137	1.97
Average for low rate		3.83 ± 0.91
Average for high rate		3.57 ± 1.43
Grand average		3.70 ± 1.1

(a) Gelman AE filters.

The results of this experiment show somewhat larger variations between individual samples than normally experienced with the laboratory rig. Three out of the four "pairs" show higher sulfate values for the lower sampling rates. However, these variations are not associated with sampling rate differences but appear to be randomly distributed amongst all samples.

Sampling Time

In this series, a set of simultaneous samples was taken in which one filter type was used to sample ambient air for 48 hours. During this time period, the same filter was used to sample each of the 24-hour halves of overall time. Two

filter types were employed; the ADL filter and the Gelman AE filter. Filter samples were analyzed for both sulfate and sulfite contents, with the results shown in Table 8.

TABLE 8. SAMPLING TIME EFFECTS

Sample Number	Filter	Mass Loading, $\mu g/m^3$	Sulfate, $\mu g/m^3$	Sulfite, $\mu g/m^3$
5A	ADL	97.8	13.3	1.4
5B	ADL	112.0	20.3	0.8
5AB	ADL	105.1	15.5	0.6
5A	AE	114.6	13.8	5.2
5B	AE	159.3	24.8	8.0
5AB	AE	107.6	20.3	0.2

It is noteworthy in the results of this run that the ambient SO_2 levels for the two 24-hour periods are appreciably different (see Appendix A). This fact appears to be reflected in the relative amounts of sulfate collected on each day, especially with the AE filter. The principal effect of sampling over the longer time period appears to be the obvious one of averaging the high and low fluctuations. The 48-hour sulfate values are close to the averages of the 24-hour samples for each filter. Sulfite values cited in Table 8 also seem to reflect some differences in basicity between the two filter types, but, in view of difficulties encountered in analysis of sulfite in these samples, the data must be considered semiquantitative at best.

SO_2 Absorption

Measurements of the absorption of SO_2 by various filter media were made under conditions similar to those encountered in ambient air sampling. Although spiking of the ambient air with SO_2 was employed in many of these runs, spiking levels were kept within the bounds of ambient levels.

A typical response curve obtained in these experiments is shown in Figure 3. Initially, the SO_2 concentration on the downstream side of the filter was close to zero. This low reading persisted for varying times depending on the nature

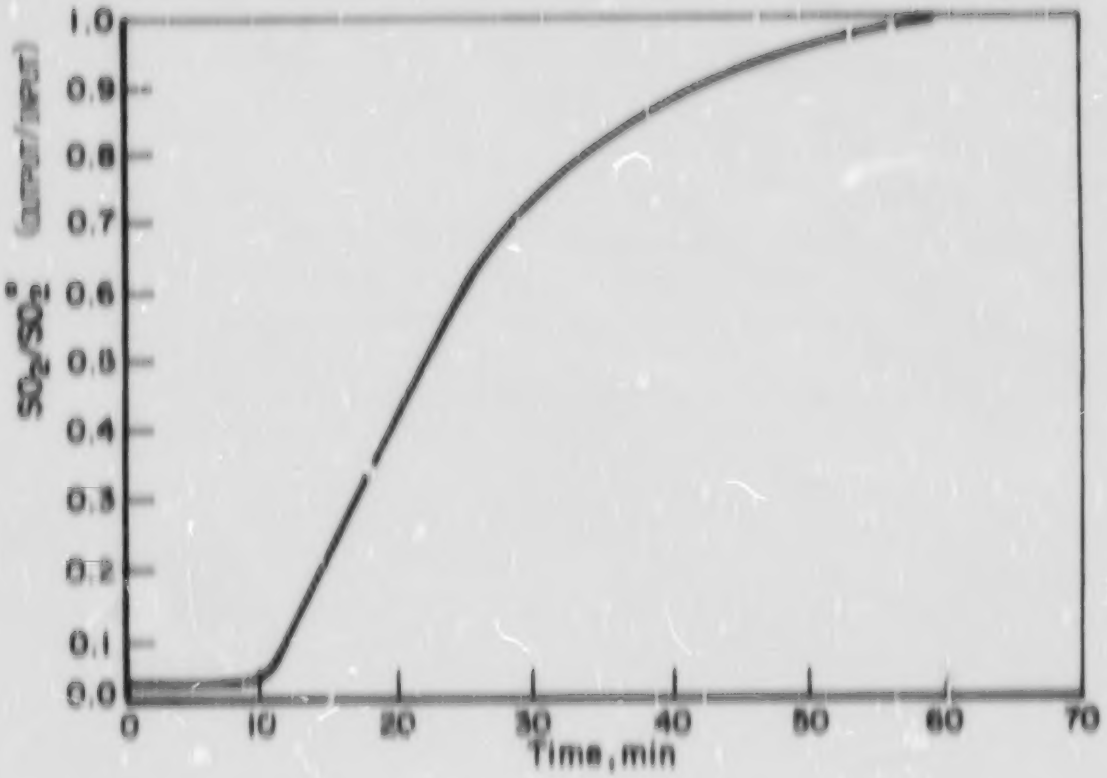

FIGURE 3. TYPICAL SO_2 RESPONSE CURVE

of the filter, the SO_2 concentration, and the relative humidity. The independent effect of temperature was not readily obvious however. After some period of time, usually of the order of 5-15 minutes for the more basic filters, breakthrough of the SO_2 was observed, and the response curve followed an S-shaped approach to the input level of SO_2. The total amount of SO_2 absorbed was calculated from knowledge of the flow rates, concentrations, and numerical integration of the response curve. Blank runs, i.e., runs without a filter in the system, also were made, and data for the filter responses were corrected for the inherent system lag. Typical blank breakthrough times were of the order of 0.1 min., and blank corrections were of the order of 16 μg SO_2. Data for the total SO_2 sorption by various filter types are given in Table 9 for comparison of different filter behaviors. It is obvious from this table that the extent of SO_2 sorption by the more basic filters (MSA 1106-BH, Gelman AE, and Gelman AA) is significantly different from that of the other filters studied. Indeed, the SO_2 responses of the acidic filters (Celotate and Pallflex E 70/2075 W) and the polymeric filters (Mitex, Fluoropore, and Polyimide) were indistinguishable from the blank. The more basic filters were therefore examined in more detail, with the results shown in Table 10.

TABLE 9. SO_2 SORPTION BY VARIOUS FILTERS

Filter Type	T, °C	RH, Percent	SO_2 Input, ppb	SO_2 Capacity, μg/cm²
MSA 1106BH	25	51	230	6.04
Gelman AE	25	48	236	8.01
Gelman AA	18	49	181	4.65
Spectrograde	25	45	236	1.08
AGL Microquartz	25	44	236	0.36
Pallflex QAST	14	60	206	0.27
Duralon	25	60	236	0.48
Pallflex E 70/2075W	20	44	150	0.00[a]
Celotate	25	65	240	0.00[a]
Polyimide	25	50	150	0.00[a]
Mitex	25	50	240	0.00[a]
Fluoropore FA	25	50	260	0.00[a]
Fluoropore FH	25	50	260	0.00[a]

(a) Indistinguishable from blank.

TABLE 10. SORPTION OF SO_2 BY BASIC FILTERS

Filter type	T, °C	RH Percent	SO_2 Input, ppb	SO_2 Capacity, $\mu g/cm^2$
MSA-1106A[a]	25	40	150	5.63
" "	25	40	298	6.99
" "	23.8	65	154	6.13
" "	25	71	310	8.57
" "	25	81	230	8.04
" "	18	81	315	7.83
" "	18	81	150	6.44
" "	18	81	305	7.98
" "	18	78	150	5.70
" "	22	61	150	6.00
" "	22	61	298	6.47
Gelman AE[b] (Batch-A)	15	93.7	298	11.55
" "	22.8	41	150	6.05
" "	24.3	34.5	300	5.41
" "	25	45	326	8.03
" "	27.8	48	140	4.85
Gelman AE[c] (Batch-B)	25.5	44	297	8.58
" "	26.8	39	300	5.48
" "	27.3	38	405	6.48
Gelman AE[c] (Batch-B)	16	71	160	4.88
" "	11.5	87.2	199	5.04
" "	12.3	79.4	269	4.46
" "	11.3	92.7	199	4.79
Gelman AA[d]	17	49	161	4.69

(a) Alkalinity = 0.21μ eq/cm^2, Blank sulfate = 9.85 $\mu g/cm^2$.
(b) Alkalinity = 0.30μ eq/cm^2, Blank sulfate = 1.1 $\mu g/cm^2$.
(c) Alkalinity = 0.30μ eq/cm^2, Blank sulfate = 4.2 $\mu g/cm^2$.
(d) Alkalinity = 0.25μ eq/cm^2, Blank sulfate = 0.39 $\mu g/cm^2$.

DISCUSSION

General Observations

Significant variations in apparent sulfate collection were observed for different filter media. These differences appear to reflect primarily chemical differences between the various filters. Mechanical factors related to sampling conditions, such as, sampling rate, and sampling time do not appear to affect the apparent sulfate collection, although, an effect due to sampling rate might well be expected. This latter parameter is discussed later in this report. Storage of filter samples under various conditions also was not observed to measurably affect the apparent sulfate collection by any given filter type. Nor was there any appreciable effect on apparent sulfate collection due to the presence of presumably active SO_2 oxidation catalysts on the filter surface. The only effect noted was caused by a possible modification of the pH of the filter medium due to the presence of some of the additives. Indeed, the principal effect leading to excess sulfur on the filter catch was due to the interaction between the filter medium and SO_2. This interaction is dependent on the SO_2 concentration, relative humidity, temperature, and the chemical nature of the filter medium.

Oxidation Catalysts

Examination of Table 6 indicates that the addition of these potentially active materials to the filter had little or no effect on the removal of SO_2. However, other investigators[6,7] used similar procedures to demonstrate that iron and manganese are catalytically active in the atmosphere. Comparison of the work of these authors with that shown above reveals three important differences:

(1) The current work was done under realistic atmospheric conditions, i.e., ambient level SO_2.

(2) The catalyst forms used in the current work were not identical to those studied previously. (It is well recognized that catalytic activity of a given substance can vary greatly depending on preparation, treatment, aging, etc. Furthermore, Cheng, et al.[7], clearly demonstrate that different chemical forms of manganese have different activities.)

(3) With the levels of SO_2 used in the above experiments, minimum rates expected from the work of Cheng, et al.[7], and Chun[6], might not be distinguishable in the short-term SO_2 sorption experiment.

Items 1 and 3 are related, and really concern the mechanism of SO_2 retention by the particles. Urone, et al.[8] measured apparent rates of the order of 4 percent/min but they do not present sufficient data for interpretation of reaction order. Cheng, et al.[7], cite a first-order mechanism, but revert to the use of gross average rates in their extrapolation to ambient conditions. There too data are insufficient for a good test of reaction order. Chun and Quon[6] suggest a capacity limited transport mechanism with no dependence on SO_2 concentration, but all of their measurements appear to lie outside of any kinetically controlled regime. Theoretical considerations by Freiberg[9] indicate a second order reaction. Problems caused by this unfortunate confusion and the lack of good kinetics data impinge not only on the sulfate sampling question but also on the general question of the fate of SO_2 in the atmosphere.

The question of reaction order is very important to any comparison of the current "catalyst" results with the earlier data mentioned above. Without a clear definition of reaction order, the earlier work cannot be extrapolated to ambient conditions. The current results do suggest that the overall reaction of SO_2 with potential catalysts is concentration dependent, and that this type of reaction does not contribute significantly to the artifact sulfate problem.

Chemistry of SO_2 Sorption by Filters

Many of the glass fiber filters commonly used for air pollution samping are known to be hygroscopic and quite basic. For example, pH's, as measured by the ASTM D 202 procedure, are generally in the range of 8-10. It therefore seems appropriate to examine the utility of the concept of absorption of SO_2 on the moist-basic surface of these filters in terms of the well-characterized chemistry of absorption of SO_2 by basic solutions.

The sorption of SO_2 in basic solutions has been studied in some detail with regard to stack-gas cleanup systems. Much of the early work traces to a series of papers published by H.F. Johnstone and co-workers during the late 1930's and early 1940's[9]. Because of the relatively unsophisticated procedures used by

Johnstone, his work has been subjected to numerous reexaminations, including a program conducted by Coutant and Levy at BCL in 1968[10]. The result is that the sorption of SO_2 by various alkaline solutions has been reasonably well characterized over a fairly wide range of the variables.

For the purpose of the discussion, the chemistry of sorption of SO_2 in basic solution can be considered in terms of the following equilibria

$$SO_2 + OH^- \rightleftharpoons HSO_3^-$$

$$HSO_3^- + OH^- \rightleftharpoons SO_3^=$$

with tacit recognition of the presence of other species such as M^+ (sodium, potassium, etc.) and $SO_4^=$ in the solution.

The equilibrium partial pressure of SO_2 in contact with such a solution is given by

$$P_{SO_2} = P = K \frac{[HSO_3^-]^2}{[SO_3^=]} \qquad (1)$$

where K is the overall equilibrium constant.

While Equation 1 accurately depicts the relationship between the equilibrium partial pressure of SO_2 and the concentrations of bisulfite and sulfite in solution, these latter parameters are not normally easily measured, especially with respect to the case of sorption on an alkaline filter. Therefore, following Johnstone's approach, we choose to make the following substitutions:

$$S = [S^{+4}] = [HSO_3^-] + [SO_3^=]$$

and, by requiring electroneutrality,

$$C = [M^+] - [OH^-] - [H^+] + 2[SO_3^=] + [HSO_3^-] + 2[SO_4^=].$$

Recognizing that, at equilibrium, $[OH^-]$ and $[H^+]$ will be relatively small compared to C and S, Equation 1 can be arranged to yield

$$P = KC \frac{(2S/C - 1 + 2[SO_4^=]/C)^2}{(1 - S/C - 2[SO_4^=]/C)}, \qquad (2)$$

Equation 2 thus gives the partial pressure of SO_2 in terms of the concentration of metal ions and the ratio of absorbed sulfur to metal ion, S/C. The term involving the ratio of sulfate to metal ion is relatively insignificant for most filter media inasmuch as bland sulfates are usually quite low. However,

this term is significant for at least one of the common filter media, and is retained here for the sake of completeness.

Equation 2 was quite satisfactory for the type of results obtained by Johnstone, and was used by him in correlation of data for a number of different kinds of alkaline solutions. However, the more precise work of Coutant and Levy showed that this type of equation fitted SO_2 equilibrium data over a wider range of variables if the C-term was replaced by $C^{2/3}$. Presumably, this form of the equation allows for variation in activity coefficients over a wider range of concentration.

Equation 2 can be rearranged and solved for S/C, the molar ratio of absorbed sulfur to metal ion in solution, with the result

$$S/C = \frac{(4-q-8z) + (q^2 + 8q - 16zq)^{1/2}}{8} \qquad (3)$$

where $q = P/KC^{2/3}$ and $z = [SO_4^=]/C$. The concentration of the solution on the surface of the filter depends on the relative humidity; the filter will tend to absorb water until the equilibrium partial pressure of water of the resulting solution is equal to the partial pressure of water in the gas phase. For many salt solutions, the relationship between the water partial pressure and salt concentration is nearly linear, and the following expression is a useful approximation:

$$\lambda C = (1 - RH) \qquad (4)$$

where λ is a characteristic constant for a particular salt, and RH is expressed as a decimal fraction. Examination of the handbook tabulations of λ and values of K given by either Johnstone or Coutant and Levy indicates that, at SO_2 partial pressures of the order of 10^2 ppb, $q \ll 1$. Therefore, Equation 3 can be simplified and combined with Equation 4 to yield

$$S/C(1-2z) = 0.5 + 0.354 \frac{P^{1/2}\lambda^{1/3}}{K^{1/2}(1-RH)^{1/3}(1-2z)^{1/2}} \qquad (5)$$

Furthermore, it is recognized that the quantity $C(1-2z)$ is equivalent to the available alkalinity of the filter as measured by ASTM D 202, with the only significant difference being that the alkalinity is determined as the number of equivalents of base rather than as number of moles of base. Therefore, if S is expressed as the number of equivalents of SO_2 absorbed,

$$S/A = 1.0 + 0.708 \frac{P^{1/2} A^{1/3}}{K^{1/2}(1-RH)^{1/3}(1-2z)^{1/2}} \quad (6)$$

Equation 6 thus indicates that the SO_2 sorption capacity of a filter should be directly proportional to the alkalinity of the filter, and should vary directly with the square root of the SO_2 partial pressure, and inversely with the cube root of (1-RH). Furthermore, the temperature dependence is implied by $K^{1/2}$, and a dependence on the blank sulfate content of the filter also is indicated. As suggested previously, this dependence on blank sulfate is insignificant for most filter media.

The nature of the base might be expected to influence the temperature coefficient of the equilibrium constant. However, Johnstone found that various bases, including sodium, potassium, ammonia, and methylamine had similar temperature coefficients. His value for the potassium system was verified by the BCL work, with K being given as

$$K = \exp [6.111 - 4232/T°K] \quad (\text{torr/mole/100 moles } H_2O). \quad (7)$$

Preliminary analysis of the data in Table 4 consisted of a statistical examination with reference to the form of Equation 6. Because of the general consistency between temperature coefficients found by Johnstone and that found in the earlier BCL work, the function given in Equation 7 was used to normalize the experimental results to 25° C. Regression techniques were then used to test the significance of the equation

$$S/A = a + b\, P^{1/2}/(1-RH)^{1/3}(1-2z)^{1/2}. \quad (8)$$

Similarly, examination was made using the square root RH function that would result from Johnstone's original formulation of the chemistry. Correlation with the cube root function was slightly better, and an overall correlation coefficient of 0.87 was determined. The results of the analysis also indicated that the presence of the constant a was statistically significant, i.e., the filters tend to absorb some minimum amount of SO_2 regardless of the exposure conditions.

A more detailed analysis of the data was then conducted using the "least-squares-cubic" procedure developed by York[12]. In applying this method, weighting factors were derived primarily from the results of the alkalinity and blank sulfate measurements which suggest uncertainties of ±7 percent in the

left- and right-hand side variables in Equation 8. A plot of the data along with the resulting least-squares values of a and b are shown in Figure 4.

These experimentally determined values of a and b can be compared with corresponding values based on the Johnstone work and that of Coutant and Levy on vapor pressures of SO_2 over potassium sulfite solutions. Using the handbook value of λ for sodium sulfate, and maintaining consistent units, the calculated value of b is 7×10^{-3}. This calculated value is only slightly more than 2σ removed from the experimental value obtained in this work. The theoretical value of the intercept is obviously considerably different from the experimental value. However, alkalinities used in reducing these data were derived by the ASTM procedure involving hot leach of the filters. As noted in Table 2, these "high temperature" alkalinities are considerably greater than alkalinities derived from ambient temperature leaching of the filters. If it is assumed that the low temperature value of the alkalinity more correctly represents the alkalinity available for SO_2 sorption during ambient sampling, the corrected value of the experimental intercept is 0.55 ± 0.13, and the theoretical value is only slightly more than 2σ removed from the experimental value. In view of the very long extrapolation required between the previous work and the current results, this "approximate agreement" seems quite good, and it seems reasonable to apply the chemical model in discussing the sorption of SO_2 on the strongly basic filter media.

Some caution is due in interpretation and application of the model at very low SO_2 concentrations. Obviously, if no SO_2 is present, there can be no SO_2 absorption. The model however implies that some finite minimum capacity for SO_2 absorption exists even at near-zero SO_2 levels, and it is assumed that the total SO_2 exposure is sufficient to satisfy that minimum capacity.

In reviewing SO_2 sorption data for other filter types, as shown in Table 5, it is obvious that the chemical model presented above does not adequately represent the performances of the weakly basic filters. With these materials, the absolute amount of SO_2 absorbed is much less than that absorbed by the strongly basic filters, but still greatly exceeds that predicted from consideration of the alkalinities. In these cases, it may be that a small amount of water vapor is absorbed by capillary condensation and that this water serves as a sorbent for the SO_2. However, direct evidence for such a phenomenon is not seen in the current work.

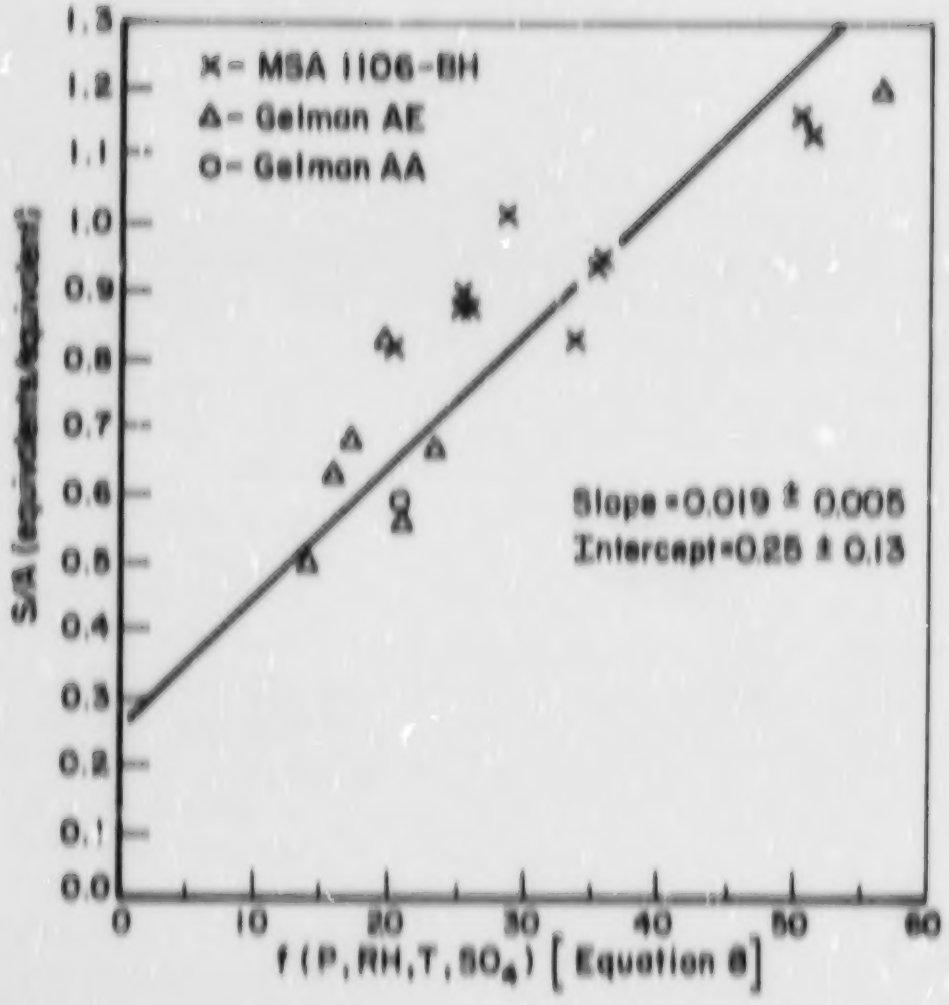

FIGURE 4. EFFECT ON FILTER AND ATMOSPHERIC VARIABLES ON SO_2 SORPTION

Oxidation of Absorbed SO_2

The oxidation of sulfites has been considered in depth by a number of workers, e.g., Beilke, et al.[13]. The reaction is highly dependent on pH, with half-lives as short as 4-5 minutes being indicated by Schroeter[14] for solutions of sodium sulfite under conditions where the rate of oxygen supply is not a limiting factor. It is, therefore, expected that the rate of oxidation of SO_2 absorbed on basic filter media is quite high, and that nearly all of the absorbed SO_2 would be oxidized within a normal 24-hour ambient sampling period. Workers at Radian[3] found this to be true, and reported conversion of about 90 percent of the absorbed SO_2 within a period of 7 hours. Sulfite contents of filter samples collected in the present work were generally low relative to the total sulfur contents of the samples, confirming the notion of rapid conversion to sulfate.

Sulfate Sampling Error

It is obvious from the above discussion that, under any given set of atmospheric sampling conditions, the absolute sulfate error per unit filter area is fixed by the available alkalinity. However, ambient sulfate levels are usually reported as mass per unit volume of air. Thus, the relative error in the measured sulfate loading is inversely proportional to the flow per unit area. For practical purposes then Equations 7 and 8 can be combined and rewritten as

$$\Delta SO_4(\mu g/m^3) = \frac{48A}{F}\left\{0.28 + 1.57 \times 10^{-5}\, e^{2116/T}\left(\frac{p^{1/2}}{(1-RH)^{1/3}(1-2z)^{1/2}}\right)\right\} \quad (9)$$

where F is the air volume per unit area (m^3/cm^2) in a 24-hour sample and the units of A are $\mu eq/cm^2$.

Table II shows a comparison of some measured excess sulfate levels with corresponding values calculated from Equation 9. These are generally in good agreement and indicate that the model can be useful in estimating excess levels of sulfate due to SO_2 absorption.

Standard Hi-Vol procedures call for use of 24-hour sampling volumes of 3-4.5 m^3/cm^2. Figure 5 shows predicted levels of sulfate sampling errors, based on Equation 9, for these sampling rates and filter alkalinities of 0.1 and 0.3 $\mu eq/cm^2$. Thus in the range of normal sampling conditions, the expected error due to SO_2 sorption on basic filters is between 0.3 and 1 $\mu g/m^3$ depending on specific conditions and sampling variables. Excursions beyond this level of error are easily conceivable however, and it is obvious that the lower the

TABLE 11. EXPERIMENTAL AND PREDICTED EXCESS SULFATES

Run No.	Filter Comparison	SO_2,(a) ppb	RH,(a) Percent	T_s,(a) K	Sulfate Difference, $\mu g/m^3$ Exp.	Cal.(b)
3A	Gelman AL-ADL(c)	90	80	286	10.7±0.8	11.3
3A	MSA-ADL(c)	90	80	286	7.2±2	8.6
10B	Gelman AA-QAST (or ADL)(c)	125	98+	298	13.6	12.8
10B	Gelman AE-QAST (or ADL)(c)	125	98+	298	16.3	17.9
11	MSA-QAST(d)	135	88	298	2.1	3.0

(a) Corresponding hourly averages selected to yield highest value for Equation 9.

(b) Calculated by Equation 9.

(c) Laboratory samples at $F = 1\ m^3/cm^2$.

(d) Standard Hi-Vol sample at $F = 3\ m^3/cm^2$.

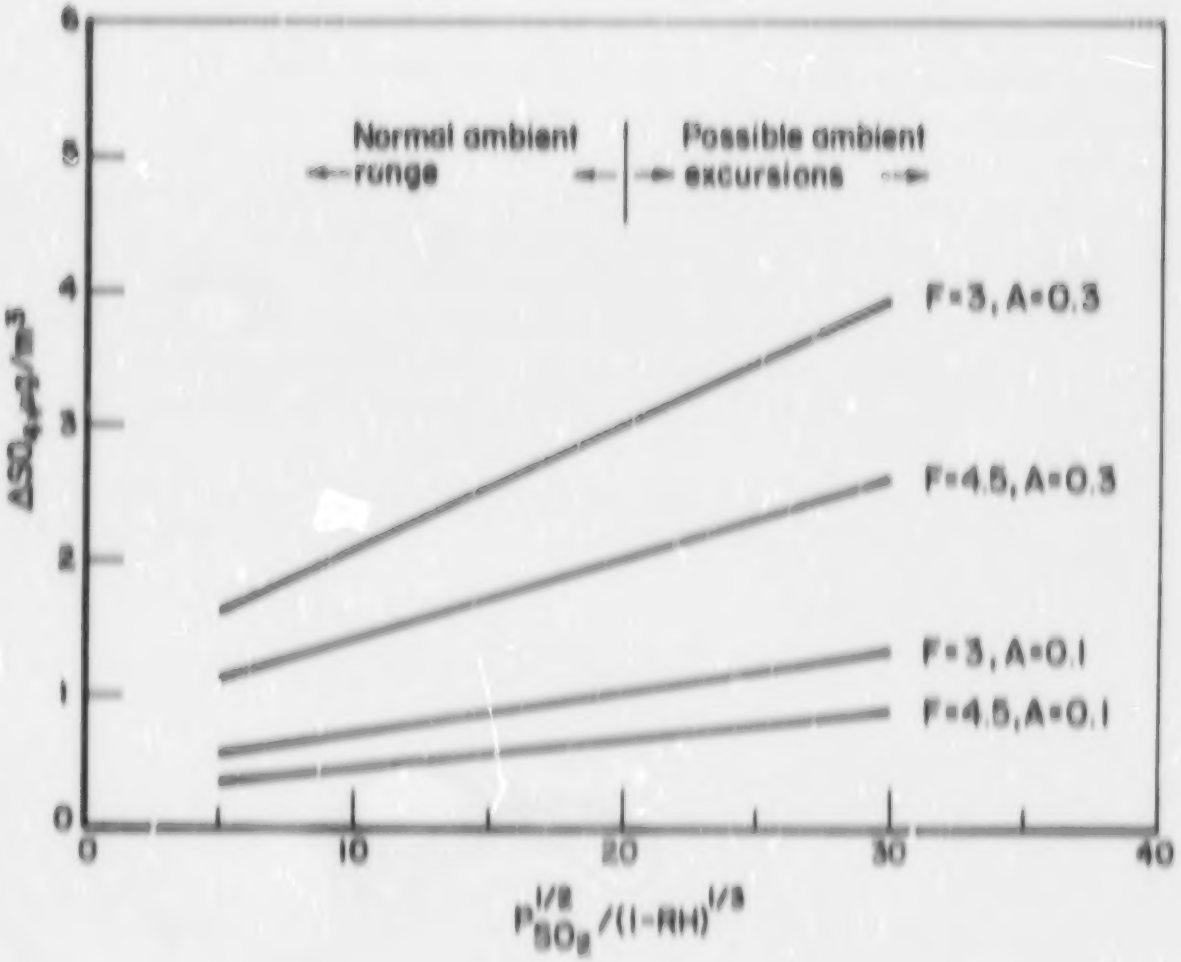

FIGURE 5. SULFATE ERROR FOR BASIC FILTERS

sampling rate, the more sensitive the error is to changing environmental conditions.

CONCLUSIONS

It is concluded that the principal error involved in sampling of ambient air for total sulfate particulate content is caused by the absorption and subsequent oxidation of ambient SO_2 in the presence of basic components of the filter medium. A model of this absorption process has been developed based on well-characterized chemistry of the sorption of SO_2 in alkaline solutions. This model relates the extent of SO_2 sorption to environmental conditions, including the relative humidity, temperature, and SO_2 concentration, and to filter characteristics, such as alkalinity and blank sulfate content. An effect due to the rate of sampling per unit area of filter is implicit in the model. The results indicate that sulfate loading errors of the order of 0.3-3 $\mu g/m^3$ can be expected with the use of common glass fiber filters, and that larger sulfate errors are possible under extreme sampling conditions. Other variables such as sampling time, storage conditions, and particulate composition appear to have no significant effect on the sulfate content of the filter catch.

SECTION 3

FIELD SAMPLING PROGRAM

OBJECTIVE

The objective of the field sampling phase of this program was an attempt to verify laboratory observations under the constraints of field sampling conditions. Specifically, experiments included comparison of representative filter types, responses of these filters to high SO_2 loads, and examination of the effects of iron- and manganese-rich particulate matter on sulfate collection.

APPROACH

The concept of simultaneous sampling was maintained in the field through the use of two standard hi-vol units joined via a common inlet duct. This modification ensured that physically and chemically similar input to each of the hi-vol units was maintained during the experiments. Stainless steel ductwork for the modified inlet was derived from the laboratory rig, with mixing orifices included for experiments involving spiking of the inlet air with SO_2.

Instrumentation for auxiliary measurements included a flame photometric SO_2 detector, an ozone chemiluminescence detector, and a chemiluminescence NO_x instrument. Measurements of temperature and relative humidity were made using wet and dry thermocouples mounted on the dual hi-vol unit. The instruments for gaseous species measurements were located with the BCL Mobile Air Sampling Van, a self-contained air-conditioned (or heated) mobile laboratory. Although this unit includes a generator for remote site operation, power for this program was obtained through the cooperation of local state, and city officials to minimize procedures needed for preserving the identity of the local air sample.

Siting

Arrangements for sampling sites used were made through the cooperation of Mr. Doug Dean, Environmental Engineer, Ohio EPA; Mr. Robert Ramhoff, Director, Mahoning-Trumbell Air Pollution Control Agency; Mr. Lou Newman, Park Manager, Pymatuning

State Park, Ohio Department of Natural Resources; the mayor of the City of Youngstown; the Youngstown Fire Department; and the Youngstown City Maintenance Department.

Fire Station No. 5--

The first site used was located at Fire Station No.5 in Youngstown. This site is routinely used for sampling of SO_2, sulfates, and total particulate. As indicated on the map shown as Figure 6, this station is located centrally with respect to the power plant and steel mill complexes of northwestern Youngstown. Historically, average SO_2, sulfate, and particulate loadings have been relatively high in this area. For example, the 1975 annual average sulfate level was approximately 20 $\mu g/m^3$.

Hi-vol sampling at this site is conducted on the roof of the fire station. At the time of our visit to this site, sampling was being conducted on every sixth day. However, during our stay, Mahoning-Trumbull Air Pollution Control Agency agreed to perform several extra hi-vol runs using their filters. Data from these runs is not available for this report, but will ultimately be available for comparison with our results. Because of space limitations at the fire station, gaseous pollutants at this site were measured in the parking lot of the Youngstown City Maintenance Department located across the street from and approximately upwind of the fire station.

Pymatuning State Park--

During the second week of the field study, hi-vol samples were collected at Pymatuning State Park, which is located approximately 35-40 miles northeast of Youngstown. Particulate measurements made by the Ohio EPA at this site traditionally show very low particulate loadings. This site is located about 25 miles from the nearest urban area.

Columbus--

During the initial stages of setup and checkout of equipment and procedures for use in the Youngstown area, several runs were made in the Columbus area, at a site removed by several miles from our laboratory facilities. This was an urban residential site obtained through the cooperation of Mr. G. William Keigley of BCL.

FIGURE 6. YOUNGSTOWN FIELD SAMPLING AREA

Experimental Plan

Four filter media were chosen for use in the field study. This are

(1) ADL quartz - This is a high-purity quartz fiber filter developed by the Arthur D. Little Co. Samples of this material were obtained through the cooperation of ADL.

(2) Pallflex QAST - This high-purity quartz fiber filter is similar in many respects to the ADL quartz, but is available commercially.

(3) MSA 1106-BH - This is a glass fiber filter that has been used extensively in both source and ambient sampling.

(4) Gelman A - The Gelman A glass fiber filter is similar to MSA 1106-BH.

The ADL filter was used as the reference filter in all experiments except those involving SO_2 spiking.

Experiments consisted of three basic types:

(1) Filter comparisons - Each of the above filters was used in one side of the dual hi-vol rig, with the ADL filter serving as the reference material on the other leg of the system. Comparisons were made during both daytime and nighttime periods for each of the filter combinations to take advantage of normal temperature and humidity trends.

(2) Catalyst effects - Several samples of the ADL filters were preloaded with either ferric oxide or manganese dioxide. These were then run in day and night experiments in comparison with clean ADL filters.

(3) SO_2 effects - Each of the filter types was run in comparison with another sample of the same type, but with one leg of the dual hi-vol spiked with additional SO_2. Again, day and night runs were made.

Experiments 1 and 2 were conducted at the Youngstown site, and all three types of experiments were conducted at the Pymatuning site.

Problem Areas

As with almost any set of experiments conducted outside of the laboratory, several problems associated with uncontrolled variables arose during the field study. The most serious of these problems was the weather. Several periods of heavy rainfall occurred during the 2-week field program. While it was possible to shield the apparatus sufficiently during a light rain to enable changing of filters, such was not possible during a heavy rain. Thus, when over 3 inches of rain fell in Youngstown during the afternoon and early evening of September 17, no experiments could be started during that period.

Although it had been expected that we might obtain a good comparison between high temperature/low humidity daytime periods and low temperature/high humidity nighttime conditions, relative humidities were generally high throughout the sampling period. This was especially true at Pymatuning where fogs or mists persisted well into the daylight hours most of the time.

Some instrumentation problems also were encountered that could not be corrected readily in the field. An electronic failure in the NO_x instrument could not be corrected, except that some periodic measurements were managed during the second week of the study. The ozone instrument also did not yield satisfactory readings when operated in the continuous mode. Thus, only periodic readings with this instrument were possible.

Analyses

All filter samples were analyzed for sulfate, sulfite, total sulfur, ammonium ion, nitrate, and total nitrogen. The ADL filters also were analyzed for metal ion content by OES in order to provide some characterization of the background particulate. Results of the nitrogen species analyses are not cited in this report, but will be included in future reports for EPA Contract No. 68-02-2213. A corresponding exchange of sulfate data from the current Los Angeles field study under the latter program has been agreed upon. Not all of the data from that program are yet available. However, results of comparison Gelman AA and QAST filters are given in Appendix C.

Sulfate analyses were performed using the Dionex ion chromatograph. Attempts at sulfite analyses by this method have not yet proven successful in our laboratory. Instead we chose to use the iodine titration procedure. This method of course yields total oxidizable content and is not specific for sulfite. Total sulfur values were obtained by micro-combustion.

RESULTS

Complete data sheets for the Columbus, Youngstown, and Pymatuning field work are given in Appendix B. These data are condensed in Table 11.

In general, the results shown in Table 11 are less than ideal; sulfite and sulfate values are consistently less than the corresponding total sulfur values (if expressed as sulfate). Apparent scatter in the data is much greater than that experienced in the laboratory measurements, and the apparent effect of the consistently wet weather is evident in the very low sulfate and particulate values on some days. However, some conclusions based on these data are possible.

DISCUSSION

The particulate loadings in this series of experiments range from a low of about 5 $\mu g/m^3$ to a high of over 300 $\mu g/m^3$. The former being observed on a rainy day at Pymatuning, and the latter being observed in Youngstown on a day when the wind was directly from a steel mill stack that appeared to be operating without particulate emission controls.

Particulate compositions at the Pymatuning and Youngstown sites are appreciably different. Those at Pymatuning represent essentially background particulate matter, while the Youngstown data show a typical steel mill emission type of particulate composition.

Inasmuch as the iodine titration procedure used for sulfite should have measured essentially all oxidizable sulfur in the filter catches, it is disturbing that the sulfate values are very much lower than the total sulfur levels. This would appear to be due to an error in the sulfate analysis procedure used for the field samples. Further evidence for this apparent deficiency is seen if a comparison is made between the calculated sulfur error (Equation 9) and the differences in sulfate, sulfite, and total sulfur levels between pairs of filters shown in Table 11. An attempt at correlation between calculated sulfur error and measured sulfite or sulfate yields correlation coefficients of 0.35 and 0.20 respectively. On the other hand, as shown in Figure 7, a correlation coefficient of 0.89 is obtained with the total sulfur values.

The data from Table 12 are further condensed and reorganized for purposes of statistical analysis in Table 13. In this reorganization the data for the sulfite measurements have been omitted. Table 14 shows a corresponding summary of the mean differences in measurements and the statistical significance of the

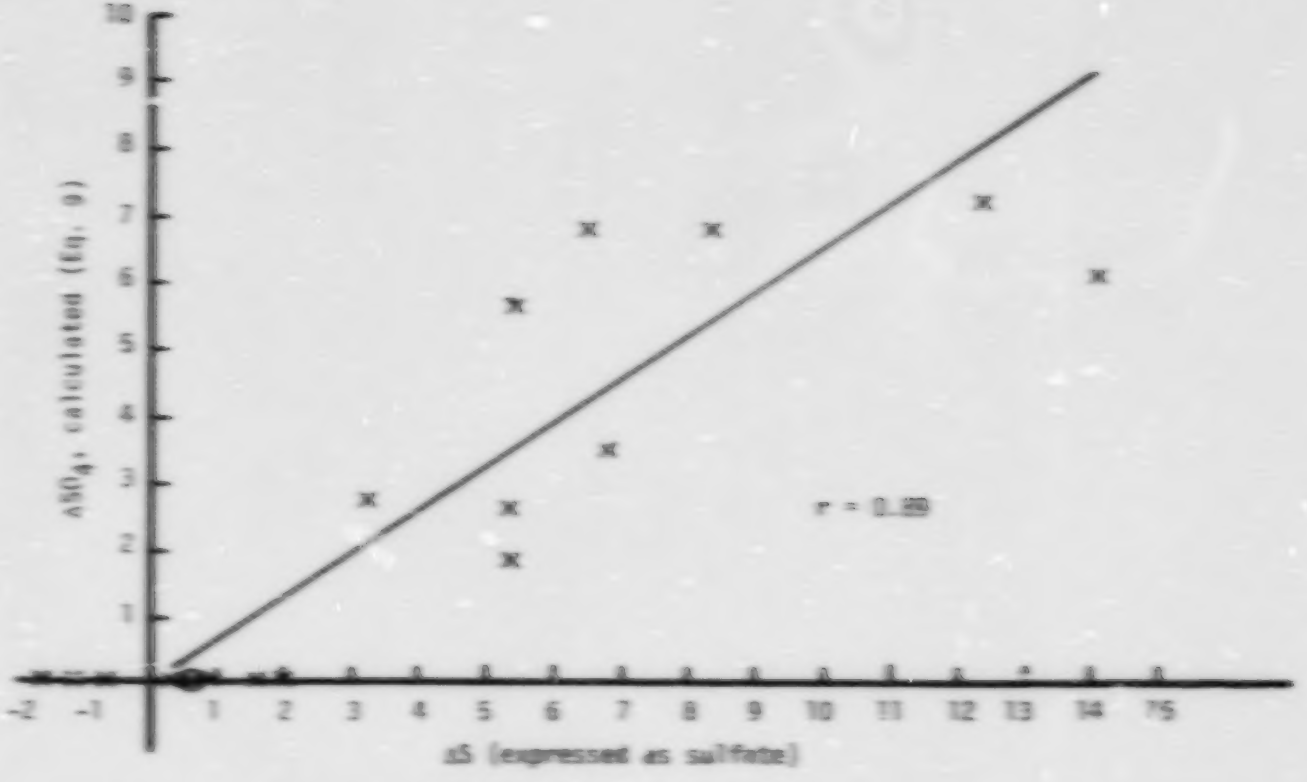

FIGURE 7. CORRELATION BETWEEN CALCULATED AND MEASURED SULFUR DIFFERENCES

TABLE 12. FIELD SAMPLE SUMMARY

Filter	Run No.	$SO_4^=$, $\mu g/m^3$	NO_3^-, $\mu g/m^3$	S, $\mu g/m^3$	Particulate, $\mu g/m^3$	Relatively High Particulate Metals					
						Fe	Mg	Pb	K	Ca	Zn
ADL	P-1a	5.8	<0.5	7.26	129.6	X		X			
Gelman A	P-1a	13.7	0.98	11.2	129.9						
ADL	P-1b	10.1	<0.2	6.3	165.2	XX		X		X	X
Gelman A	P-1b	13.2	0.4	8.1	159.9						
ADL	P-1c	11.39	<0.2	8.29	175.4	X		X			X
GPST	P-1d	11.73	<0.2	7.76	170.0						
ADL	P-1d	2.1	<0.2	2.5	51.5	X		X			X
GPST	P-1d	3.1	1.5	2.8	47.9						
ADL	P-1e	0.35	<0.4	1.3	23.9			X			X
MSA	P-1e	0.22	<0.4	3.1	30.4						
ADL	P-1f	9.53	1.0	1.7	27.6			X			X
MSA	P-1f	6.68	0.4	3.88	31.4						
ADL	P-1g	3.35	0.4	3.02	95.0	X	X	X		X	X
ADL + MnO_2	P-1g	1.91	0.2	3.95	60.0						
ADL	P-1h	5.54	1.48	5.77	188.7	XX	X	X		X	X
ADL + MnO_2	P-1h	7.50	<0.2	7.40	175.7						
ADL	P-1i	6.75	0.5	6.41	331.0	XX	X	X	X	X	X
ADL + Fe_2O_3	P-1i	5.48	<0.2	6.78	273.7						
ADL	P-1a	5.42	0.4	6.71	56.4						
Gelman A	P-1a	3.14	<0.4	6.71	45.9						
ADL	P-1b	4.75	2.4	4.64	41.8						
Gelman A	P-1b	5.64	1.0	7.53	39.2						
ADL	P-1c	0.1	0.45	1.13	11.8						
GPST	P-1c	0.88	1.0	0.9	11.6						
ADL	P-1d	0.33	1.01	0.68	13.9						
GPST	P-1d	0.20	0.45	0.90	11.9						
ADL	P-1e	(-0.3)	1.5	0.34	6.1						
MSA	P-1e	1.88	1.0	4.4	9.3						
ADL	P-1f	0.0	0.45	0.26	15.4						
MSA	P-1f	4.69	1.90	5.28	18.5						

TABLE 12. CONTINUED

Filter	Run No.	$SO_4^=$, $\mu g/m^3$	SO_2, $\mu g/m^3$	S, $\mu g/m^3$	Particulate, $\mu g/m^3$	Relatively High Particulate Metals					
						Fe	Mg	Pb	K	Ca	Zn
ADL	P-1g	1.09	0.4	1.76	26.2						
ADL + MnO_2	P-1g	1.86	0.4	2.20	29.1						
ADL	P-1e	1.02	1.49	1.60	30.3						
ADL + MnO_2	P-1e	2.05	0.45	2.29	30.9						
ADL	P-1i	(-0.1)	1.44	0.33	12.1						
ADL + Fe_2O_3	P-1i	(-0.2)	1.01	0.56	12.3						
ADL	P-1j	(-0.35)	0.45	0.00	5.5						
ADL + Fe_2O_3	P-1j	(-0.35)	0.45	0.11	4.8						
MSA	P-2a	(-1.1)	<0.5	2.86	17.1						
MSA	P-2a	0.0	1.0	2.06	14.6						
Gelman A	P-2b	4.0	1.93	4.08	36.0						
Gelman A	P-2b	2.89	2.40	3.65	33.3						
GAST	P-2c	2.11	2.36	2.70	34.2						
GAST	P-2c	1.44	2.36	1.80	30.7						
ADL	P-2d	2.24	1.92	3.16	34.1						
ADL	P-2d	2.35	1.91	3.71	33.8						
ADL	C-1	0.55	0.11	1.46	54.9						
MSA	C-1	0.57	0.55	3.74	56.4						
ADL	C-2	3.50	1.13	3.96	83.0						
MSA	C-2	3.52	0.56	5.07	87.1						
GAST	C-3	10.9	—	—	101.6						
MSA	C-3	7.86	—	—	75.2						

TABLE 13. FIELD SAMPLE DATA

Variable	Site	Comparison Group									
		ADL vs Gilman A		ADL vs DIST		ADL vs MSA		ADL + MnO_2		ADL + Fe_2O_3	
SO_4, mg/m^3	Youngstown	5.80 10.70	13.70 13.20	11.20 2.10	11.73 3.10	6.35 9.53	0.22 6.68	3.55 5.54	1.91 7.50	6.75	5.48
	Pynotuning	5.42 4.75	5.14 5.64	0.70 0.33	0.88 0.20	-0.30 0.00	1.88 4.69	1.09 1.02	1.96 2.85	-0.70 -0.35	-0.20 -0.35
	Columbus					0.66 1.50	0.57 3.52				
S, mg/m^3	Youngstown	7.28 6.30	11.20 8.10	8.29 2.50	7.76 2.80	1.30 1.70	3.10 5.77	3.02 7.40	3.95	6.41	6.78
	Pynotuning	6.71 4.64	6.71 7.46	1.13 0.68	0.90 0.90	0.34 1.56	4.40 5.28	1.76 1.60	2.20 2.26	0.33 0.00	0.56 0.71
	Columbus					1.46 1.96	3.74 5.07				
Particulates, mg/m^3	Columbus	129.6 165.2	129.9 159.9	175.4 91.5	170.0 47.9	23.9 27.6	30.4 37.4	55.0 188.7	60.3 175.7	331.0	273.7
	Pynotuning	56.4 41.7	45.9 38.2	11.8 13.8	11.6 11.9	6.1 15.4	9.3 18.5	28.2 30.3	25.1 30.9	12.1 5.5	12.3 4.8
	Columbus					54.9 83.0	56.4 87.1				

TABLE 14. STATISTICAL COMPARISON OF AQL FILTER PERFORMANCE WITH OTHER FILTERS

Site	Variable	AQL Filter Versus					
		Gelman A	GAST	MSA	AQL + MnO_2	AQL + Fe_2O_3	All 5
Youngstown	Number of Pairs	2	2	2	2	1	9
	SO_4, $\mu g/m^3$	-6.58	-0.67	1.49	-0.35	1.27	-0.96
	S, $\mu g/m^3$	-2.66	0.12	-1.99[a]	-1.28	-0.37	-1.38[b]
	Particulate, $\mu g/m^3$	2.50	4.50	-6.75	4.00	57.38	7.67
Pyrotuning	Number of Pairs	2	2	2	2	2	10
	SO_4, $\mu g/m^3$	-0.38	-0.32	-2.44	-0.90[a]	-0.05	-0.98[a]
	S, $\mu g/m^3$	-1.40	0.01	-4.39[b]	-0.57	-0.17	-1.38[a]
	Particulate, $\mu g/m^3$	6.55	7.19	-1.75[b]	-0.75	0.25	0.85
All Field Samples	Number of Pairs	4	4	6	4	3	21
	SO_4, $\mu g/m^3$	-2.90	-0.50	-0.64	-0.59	0.46	-0.67[a]
	S, $\mu g/m^3$	-2.13[a]	0.61	-2.69[b]	-0.92[a]	-0.24[a]	-1.37[b]
	Particulate, $\mu g/m^3$	4.52	2.80[a]	-3.68[b]	1.62	19.37	2.48

(a) Statistically significant at the 10% significance level (90% confidence level).

(b) Statistically significant at the 5% significance level (95% confidence level).

data is presented. The data were analyzed using Student's t-test where the data were considered as paired observations. That is, comparisonsare made between the ADL reference filter and the test filter for each experiment. This pairing reduces extraneous influences on the subsequent measurements, and results in a more powerful test. The t-test tests the hypothesis that the mean difference is zero.

Separate statistical tests were run for each comparison group in Table 12. The data were tested for the two sites individually and collectively. In examining the mean differences for statistical significance, no strong patterns emerge from consideration of the individual sites. At the Youngstown site, significantly higher sulfur values were obtained with the MSA filter than with the ADL filter, and this significance also was noted when the ADL filter was compared with the aggregate of all of the other filters. At Pymatuning, the sulfate measurements were significantly higher with the MnO_2-treated ADL filter, and this significance is repeated in comparing the ADL filter with the aggregate of samples. Total particulate measurements at Pymatuning were significantly higher for the MSA filter than for the ADL.

When the data were combined across sites, the ADL filters consistently yielded significantly smaller measures of sulfur than the other filter types, with the exception of the QAST filter. This observation is the strongest pattern to emerge from the data.

Because of the limited number of samples and variety of experiments conducted on this program, the number of observations for a statistical test is quite small. This, of course, limits the power of the test to detect significant trends. From a statistical viewpoint, the trends suggested in Table 13 should be considered indicative, but not necessarily conclusive.

CONCLUSIONS

The objective of the field program phase of this work was to attempt to verify laboratory observations under the constraints of field operating conditions. In a limited sense, this has been accomplished. The relatively clean ADL and QAST quartz filters do yield lower sulfur levels than the more alkaline glass fiber filters that display a tendency for sorption of SO_2. Furthermore, differences in apparent sulfur collections correlate well with values predicted by the results of the laboratory measurements. The field data do suggest that the presence of MnO_2 and possibly Fe_2O_3 can influence the apparent ambient

sulfur loading. This is in contrast with the laboratory measurements indicating no significant effect. This may be indicative of an interaction that is sensitive to other parameters that have not been recognized. It would seem that this question should be investigated further. In any case, it seems probable that the filter itself would not be involved in that interaction.

SECTION 4

RECOMMENDATIONS

The observations made on this program indicate that the most serious cause of ambient sulfate error, absorption of SO_2, can be avoided through proper choice of filter media. The best filter medium is one that is free of alkaline impurities and has a low blank sulfate. From the standpoint of good analytical practice, blank contents of all impurities should be as low as possible. Adherence to such a criterion would permit more accurate analysis of the general composition of the filter catch. Several filters meet these general criteria: ADL Microquartz, Pallflex QAST, Pallflex E 70/2075-W, Mitex, Fluoropore, and Celotate. These are not the only criteria however for filter media that are to be used in a routine fashion for remote (nonlaboratory) sampling, in an air pollution surveillance network.

At very least, the following additional criteria need to be considered:

(1) The collection efficiency for submicron particles should be 99+ percent.

(2) The pressure-drop across the filter should not change markedly with normal particulate loadings.

(3) Mechanical strength must be sufficient to enable handling, mounting, demounting, and possibly folding of the filter without appreciable loss of filter weight due to flaking, shedding, or adhesion to contacted surfaces.

(4) Unit cost must not prohibit large volume usage.

To the best of our knowledge, all of the above filter media except Mitex[15] can be obtained in types that meet the first criterion. The second criterion is probably most important with respect to the use of the filter in conventional 24-hour hi-vol sampling. With membrane filters such as the Mitex, Fluoropore, and Celotape, pressure-drop changes tend to be high and nonlinear with accumulation of large quantities of particulate material on the filter surface. Accurate

definition of flow rate changes becomes difficult under these conditions, and samples can become biased with respect to the early portion of the sampling period. In special cases, where shorter sampling periods are employed, the second criterion is not as important.

The third criterion deals with a problem normally inherent in fibrous filters such as the glass and quartz materials. In general, these filters do tend to shed fiber fragments especially when the fiber length is very small.

The unit cost of the Teflon filters is very high compared to that of the other filter media. Because of the high cost and pressure-drop characteristics of these filters, their use is probably best suited to short-term sampling with sampling devices using filter sizes smaller than the conventional 8 x 10 hi-vol filters.

At this point, the quartz fiber filters would seem to be the best choices for conventional hi-vol sampling. If and when other high purity silica filters become commercially available, they also should be considered.

While the current work suggests that these filter media would be suitable for general hi-vol sampling of sulfates, additional data should be obtained under extended field operational conditions. It is recommended that simultaneous sampling with these filter media be conducted at selected air pollution monitoring sites. These sites should be chosen with a view towards representing as wide a range of typical ambient conditions as possible. Design of the experiment should include statistical considerations to ensure adequate recognition of the variables. Furthermore, inasmuch as sampling methods other than the conventional hi-vol system are being used by EPA personnel for special purpose sampling, it seems advisable to include the use of those sampling systems in the overall program. For example, the dichotomous sampler and the tape sampler used for aerial sulfate sampling should be included in this field methodology evaluation program. With the current program serving as a base, such an extended-term field program would contribute significantly towards validation of ambient sulfate monitoring practices. Of course, other pollutants, such as, nitrates should be included in the overall scheme.

REFERENCES

1. Frank, N.H., Temporal and Spatial Relationships of Sulfates, Total Suspended Particles, and Sulfur Dioxide. In: Proceedings of the 67th Annual Meeting of the Air Pollution Control Association, Denver, June, 1974.

2. Lee, R.E., Jr. and Wagman, J., A Sampling Anomaly in the Determination of Atmospheric Sulfate Concentration, Am. Ind. Hyg. J., 27:266, 1966.

3. Radian Corporation Final Report to Electric Power Research Institute, Sulfur Dioxide Interferences in the Measurement of Ambient Particulate Sulfate, January, 1976 (EPRI 262).

4. Pierson, W.R., Hammerle, R.H., and Brachaczek, W., Sulfate Formed by Interaction of Sulfur Dioxide with Filters and Aerosol Deposits, Anal. Chem., 48:1808, 1976.

5. Novakov, T., Chang, S.G., and Harker, A.B., Sulfates as Pollution Particulates: Catalytic Formation on Carbon (Soot) Particles, Science, 186:259, 1974.

6. Chun, K.C. and Quon, J.E., Capacity of Ferric Oxide Particles to Oxidize Sulfur Dioxide in Air, ES&T, 7:532-538, 1973.

7. Cheng, R.T., Corn, M., and Frohliger, B.L., Contribution to the Reaction Kinetics of Water Soluble Aerosols and SO_2 in Air at ppm Concentrations, Atmos. Environ., 5:987-1008, 1971.

8. Urone, P., Lutspe, H., Noyes, C.M., and Parker, J.E., Static Studies of Sulfur Dioxide Reactions in Air, ES&T 2:611-618, 1968.

9. Freiberg, J., Effects of Relative Humidity and Temperature on Iron-Catalyzed Oxidation of SO_2 in Atmospheric Aerosols, ES&T, 8:731-734, 1974.

10. Johnstone, H.F., Recovery of Sulfur Dioxide From Waste Gases-Equilibrium Particle Pressures Over Solutions of the Ammonia-Sulfur Dioxide-Water System, Ind. Eng. Chem., 27:587, 1935; Ibid 30:101, 1938.

11. Coutant, R.W. and Levy, A., Study of Phase Equilibrium in Selected SO_2 Sorbent Systems, unpublished report, data available on request.

12. York, D., Least-Squares Fitting of a Straight Line, Can. J. Phys., 44:1079, 1966.

13. Dwilke, S., Lamb, D., and Muller, J., On the Uncatalyzed Oxidation of Atmospheric SO_2 by Oxygen in Aqueous Systems, Atmos. Environ., 9:1083, 1975.

14. Schroeter, L.C., J. Pharm. Sci., 52:559, 1963.

15. Liu, B.Y.H. and Lee, K.W., Efficiency of Membrane and Nuclepore Filters for Submicrometer Aerosols, ES&T, 10:345-350, 1976.

APPENDIX A

GAS COMPOSITION DATA

Tables A-1 through A-9 show hourly averages of various ambient gaseous pollutant levels for selected 24-hour laboratory experiments.

TABLE A-1. GAS COMPOSITION DATA[a]
RUN 2B

Hour	O_3[b]	SO_2 L[c]	SO_2 R[c]	NO	NO_2	NO_x	T, °K	RH, %
1	140	199	47	3	32	35	302	61
2	163	219	58	14	44	58	303	60
3	186	213	63	4	39	43	303	61
4	225	212	72	7	37	44	302	65
5	252	201	86	5	46	51	301	69
6	270	209	89	4	47	51	301	64
7	325	213	95	5	47	52	300	69
8	338	208	95	5	55	61	300	69
9	362	206	95	4	30	34	292	69
10	359	210	92	5	29	34	291	68
11	348	205	91	5	24	29	291	76
12	348	203	91	2	24	26	291	76
13	339	205	93	5	32	37	291	78
14	323	203	93	7	53	60	291	85
15	316	206	89	17	59	76	291	87
16	289	206	89	23	66	89	290	81
17	176	203	68	103	74	177	290	77
18	121	209	60	225	95	330	290	73
19	110	245	78	160	75	235	289	66
20	116	250	83	32	68	100	290	60
21	136	236	85	9	45	54	290	57
22	147	232	72	6	37	43	291	54
23	170	225	69	2	37	39	291	53
24	180	232	66	2	29	31	291	52
24-hour average	240	214±14	80±14	27	47	75	298	66

(a) ppb unless otherwise noted.

(b) Variables other than SO_2 are the same in both branches.

(c) Left and right system branches.

TABLE A-2. GAS COMPOSITION DATA[a]
RUN 3A

Hour	O_3	SO_2	NO	NO_2	NO_x	T, °K	RH, %
1	88.0	86.1	73.6	2.0	77.5	290.0	55.6
2	115.0	83.9	84.5	3.0	87.5	290.0	56.7
3	130.0	92.4	92.0	3.5	95.5	290.3	55.9
4	155.0	93.6	100.5	5.5	106.0	290.5	55.9
5	157.5	97.0	106.0	7.3	113.3	289.9	59.1
6	160.0	95.9	110.5	7.0	117.5	289.3	62.3
7	160.0	94.8	119.0	5.3	124.3	289.0	63.2
8	160.0	95.9	125.0	6.5	131.5	288.6	65.5
9	157.5	91.2	128.5	6.0	134.5	287.6	70.2
10	150.0	91.2	135.0	5.0	140.0	287.0	72.0
11	147.5	88.9	140.0	7.3	147.3	286.9	72.3
12	150.3	88.8	147.0	7.5	154.5	286.5	74.8
13	147.5	90.1	153.5	7.5	161.0	286.5	73.9
14	140.0	91.2	159.0	7.5	166.5	286.0	77.7
15	137.5	90.1	162.5	8.3	170.8	286.0	77.9
16	130.0	86.4	167.0	8.5	175.5	285.8	80.1
17	120.0	85.1	173.0	6.5	179.5	285.6	81.8
18	110.0	86.4	180.0	10.5	190.5	286.1	74.8
19	110.0	78.5	182.0	7.5	189.5	286.6	74.9
20	115.0	83.9	184.5	8.0	192.5	287.4	69.6
21	135.0	86.4	187.5	8.5	196.0	288.5	64.2
22	140.0	86.4	193.5	9.0	202.5	289.4	61.2
23	165.0	87.6	196.3	8.3	204.5	289.7	60.2
24	175.0	88.9	197.5	9.5	207.0	290.1	58.4
24-hour average	138.5	89.1	143.8	6.7	150.5	288.1	67.3

(a) ppb unless otherwise noted.

TABLE A-3. GAS COMPOSITION DATA[a]
RUN 5A

Hour	O_3	SO_2	NO	NO_2	NO_x	T, °K	RH, %
1	0	60	22	11	31	292	30
2	0	65	11	15	24	295	26
3	15	66	5	12	16	296	26
4	80	69	7	11	17	297	23
5	80	76	13	13	23	297	23
6	80	68	11	19	29	297	22
7	65	60	18	25	44	297	22
8	80	71	53	20	74	297	22
9	95	70	75	17	97	296	24
10	97	81	184	17	204	296	26
11	102	78	289	14	315	294	26
12	102	78	275	15	298	293	28
13	100	81	274	24	309	293	26
14	107	89	223	20	254	292	30
15	105	84	233	23	265	291	29
16	117	84	308	18	340	290	34
17	120	86	300	17	328	289	33
18	122	85	265	25	287	290	32
19	120	84	252	15	276	289	36
20	105	78	240	16	264	291	30
21	100	78	311	16	330	290	36
22	95	81	352	17	387	292	30
23	65	86	175	25	207	292	31
24	85	85	48	25	74	296	25
24-hour average	87	77	165	18	180	293	28

(a) ppb unless otherwise noted.

(b) 10:30 a.m.

TABLE A-4. GAS COMPOSITION DATA[a]
RUN 58

Hour	O_3	SO_2	NO	NO_2	NO_x	T, °K	RH, %
1[b]	20	63	15	19	36	299	20
2	40	59	13	17	37	299	19
3	25	60	14	17	32	298	21
4	47	86	39	24	65	297	21
5	85	63	34	23	60	297	22
6	72	89	72	21	102	297	23
7	100	93	126	17	149	295	24
8	90	105	64	21	88	295	26
9	115	144	84	26	115	294	27
10	132	154	77	16	98	294	28
11	125	93	29	19	52	294	27
12	112	156	30	18	51	293	29
13	170	124	19	17	37	291	35
14	150	122	16	16	34	291	34
15	160	125	21	17	39	291	34
16	132	123	36	15	53	292	31
17	135	89	52	15	64	292	34
18	42	64	63	15	84	292	33
19	0	147	40	18	61	291	33
20	95	225	31	15	51	291	35
21	80	202	32	18	53	292	78
22	80	144	22	12	33	293	73
23	80	382	32	18	53	292	75
24	82	211	27	17	45	291	46
24-hour average	90	130	41	18	62	294	34

(a) ppb unless otherwise noted.

(b) 11:00 a.m.

TABLE A-5. GAS COMPOSITION DATA[a]
RUN 6A

Hour	O_3	SO_2	NO	NO_2	NO_x	T, °K	RH, %
1[b]	66	66	10	9	13	279	36
2	77	96	11	4	13	279	38
3	90	86	8	6	11	279	40
4	102	84	9	12	12	279	39
5	100	96	8	13	11	280	31
6	100	91	9	15	13	281	29
7	95	84	9	13	13	281	29
8	105	86	9	13	14	280	28
9	120	89	13	15	17	279	29
10	132	88	8	15	13	279	29
11	125	91	9	14	13	279	29
12	127	89	7	10	10	279	28
13	120	89	8	10	10	279	30
14	120	86	7	9	10	279	30
15	120	84	7	8	10	278	30
16	120	85	7	8	9	278	31
17	115	84	7	5	9	278	31
18	122	85	7	6	9	277	33
19	120	86	6	4	8	277	34
20	120	85	7	5	8	277	32
21	126	78	7	7	9	277	34
22	117	86	9	13	12	277	33
23	90	81	14	12	20	277	33
24	87	81	21	16	24	278	32
24-hour average	110	87	9	10	12	279	32

(a) ppb unless otherwise noted.

(b) 2:30 p.m.

TABLE A-6. GAS COMPOSITION DATA[a]
RUN 7

Hour	O_3	SO_2	NO	NO_2	NO_x	T, °K	RH, %
1	72.5	66.5	6.3	16.8	17.5	286.4	81.4
2	90.0	36.2	0	9.0	6.0	289.6	76.3
3	110.0	43.9	0	9.8	6.5	289.9	78.8
4	130.0	50.9	0	5.5	0	290.3	74.5
5	135.0	55.4	0	6.0	0	290.1	78.3
6	145.0	59.1	0	4.0	0	288.6	79.2
7	137.5	59.1	0	10.8	8.0	286.8	84.1
8	140.0	51.7	0	5.5	1.5	286.8	81.8
9	140.0	53.3	0	8.3	3.3	285.6	79.1
10	140.0	55.6	0	10.5	6.0	284.4	76.2
11	142.5	54.3	0	12.5	6.5	283.5	75.5
12	140.0	63.0	0	7.5	2.5	282.9	72.2
13	137.5	59.5	0	4.5	0.5	282.5	68.3
14	125.0	63.0	0	4.0	0	281.9	77.1
15	130.0	57.6	0	4.5	0	282.4	73.1
16	125.0	51.1	0	2.0	0	282.1	72.9
17	102.5	66.3	0	6.5	0.5	281.3	72.1
18	105.0	61.8	0	8.5	2.5	280.5	74.4
19	90.0	62.9	0	11.5	10.8	280.3	74.2
20	105.0	63.1	4.0	11.0	16.5	280.1	75.5
21	100.0	84.8	24.3	13.0	38.5	280.3	74.9
22	65.0	100.1	59.5	23.0	89.0	280.5	75.9
23	60.0	115.8	28.8	11.5	44.5	281.1	75.7
24	60.0	44.8	15.5	6.0	24.0	283.0	75.2
24-hour average	113.5	62.9	5.6	9.1	12.3	284.3	76.2

(a) ppb unless otherwise noted.

TABLE A-7. GAS COMPOSITION DATA[a]
RUN 8

Hour	O_3	SO_2	NO	NO_2	NO_x	T, °K	RH, %
1	157.5	55.6	8.3	7.5	16.0	289.9	64.5
2	185.0	69.6	7.5	6.0	14.0	290.9	65.4
3	227.5	67.8	7.5	13.8	23.0	291.4	64.8
4	245.0	81.2	9.0	15.0	25.5	291.5	64.9
5	245.0	79.7	6.8	18.0	26.3	290.3	68.6
6	245.0	78.5	7.0	16.0	24.0	289.3	68.2
7	262.5	79.8	7.0	17.8	27.3	288.3	69.5
8	260.0	69.6	10.5	23.5	36.5	287.6	69.0
9	247.5	77.8	8.5	21.3	32.0	287.3	71.0
10	240.0	69.6	9.5	23.0	35.5	286.4	73.9
11	247.5	72.7	10.6	21.5	34.0	285.7	75.3
12	240.0	75.6	4.0	18.5	24.5	285.5	73.2
13	245.0	77.0	3.8	16.0	20.8	284.8	75.9
14	240.0	93.2	4.0	15.0	20.5	284.5	81.8
15	235.0	236.1	9.3	19.0	32.0	236.1	82.2
16	225.0	230.1	14.5	23.0	40.0	284.0	80.1
17	227.5	199.5	17.5	25.5	43.5	284.1	79.5
18	235.0	176.5	27.0	23.0	52.5	284.3	76.1
19	117.5	262.7	57.8	24.8	88.0	284.1	79.5
20	10.0	105.2	36.5	15.0	61.5	285.1	76.8
21	30.0	78.3	16.8	14.8	33.3	287.3	74.7
22	40.0	78.3	14.0	14.0	35.0	286.3	75.6
23	55.0	80.3	10.5	9.5	24.5	290.3	71.2
24	65.0	83.7	9.0	8.0	18.0	290.6	72.6
24-hour average	189.0	110.0	13.4	17.1	33.0	287.3	73.1

(a) ppb unless otherwise noted.

TABLE A-8. GAS COMPOSITION DATA[a]
RUN 108

Hour	O_3	SO_2	NO[b]	NO_2[b]	NO_x	T, °K	RH, %
1	42.0	60.7			22.3	301.0	92.1
2	65.0	69.6			15.5	299.5	97.1
3	97.5	79.8			10.8	299.6	98.5
4	125.0	83.9			12.5	300.4	97.1
5	175.0	102.1			12.3	299.9	99.0
6	225.0	112.3			8.0	299.5	100.0
7	235.0	126.6			17.5	299.5	99.0
8	270.0	114.4			2.5	296.3	100.0
9	287.5	119.9			8.3	296.9	100.0
10	290.0	119.9			15.5	296.9	100.0
11	300.0	120.8			22.5	297.0	100.0
12	300.0	118.1			9.0	296.8	100.0
13	305.0	119.9			5.3	297.3	97.5
14	320.0	123.4			7.5	297.5	98.0
15	327.5	125.1			3.8	297.5	98.9
16	335.0	126.9			7.5	297.4	94.9
17	315.0	120.2			38.3	296.6	100.0
18	230.0	95.9			60.0	296.5	99.0
19	165.0	92.0			49.8	297.8	98.0
20	160.0	148.5			42.0	299.8	92.3
21	180.0	92.4			15.5	301.9	90.0
22	200.0	98.1			13.0	304.0	86.1
23	217.5	99.2			11.3	304.6	87.4
24	215.0	95.9			8.5	305.3	86.4
24-hour average	219.4	106.1			17.4	299.2	96.2

(a) ppb unless otherwise noted.

(b) Questionable data.

TABLE A-9. GAS COMPOSITION DATA[a]
RUN 11A

Hour	O_3	SO_2	NO[b]	NO_2[b]	NO_x	T, °K	RH, %
1	195.0	85.6			24.8	304.4	79.3
2	230.0	86.4			36.5	304.9	82.2
3	250.0	87.6			32.0	303.3	84.1
4	285.0	104.3			28.0	305.3	80.7
5	345.0	110.6			24.8	301.3	91.4
6	355.0	112.5			38.0	303.5	84.3
7	375.0	115.3			45.8	302.7	84.4
8	400.0	119.9			49.5	302.1	86.4
9	427.5	125.1			37.0	301.3	86.7
10	445.0	125.2			48.0	300.5	86.9
11	450.0	129.4			51.0	300.2	86.8
12	470.0	131.9			86.0	299.9	89.5
13	507.5	135.1			28.3	298.8	88.8
14	520.0	135.1			14.5	298.8	88.3
15	525.0	142.5			26.0	298.5	88.3
16	535.0	136.6			28.0	298.1	89.2
17	415.0	108.3			54.0	297.6	87.1
18	290.0	88.9			57.0	298.4	86.4
19	245.0	88.9			83.0	298.3	87.8
20	250.0	88.9			25.5	297.6	89.0
21	240.0	85.1			39.0	297.5	87.6
22	240.0	83.9			71.0	298.4	88.3
23	247.5	85.1			30.3	300.3	84.5
24	250.0	81.2			27.5	301.0	85.3
24-hour average	353.2	107.8			40.4	300.5	86.3

(a) ppb unless otherwise noted.

(b) Questionable data.

APPENDIX B

FIELD SAMPLING DATA

Table B-1 shows particulate compositions for samples collected on the field program. In most cases, only the ADL numbers of the filter pair was analyzed. However, in experiments P-2a and P-2b where the ADL filter was not employed, the analyses were performed on the Gelman A and MSA-1106-BH filters. Data for those cases are not corrected for filter blanks.

Tables B-2, etc., show sampling conditions for the various field experiments.

59

Table B-2. Field Atmospheric Conditions

Site Youngstown, OH
Date 9-14-76
Exp. No. Y-1a

Flow Rates:
A 44.1 cfm
B 43.9 cfm

Filters:
A ADL
B Gelman A

Sample Time 5.50 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	102	24	59	120		
2	121	24	53	100		
3	155	24	54	110		
4	134	26	51	180		
5	157	26	49	350		
6						
7						
8						
9						
10						
11						
12						

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	129.6	6.80	<0.5	7.28
B	129.9	13.7	0.98	11.2

Comments: Afternoon run, NO$_x$ instrument not working, ozone instrument questionable.

Table B-3. Field Atmospheric Conditions

Site Youngstown, OH
Date 9-14/15-76
Exp. No. Y-1b

Flow Rates:
A 44.9 cfm
B 44.8 cfm

Filters:
A ADL
B Gelman A

Sample Time 12.00 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	94	26	44			
2	79	26	48			
3	112	26	48			
4	126	26	50			
5	133	26	54			
6	139	26	55			
7	149	26	54			
8	147	26	55			
9	142	26	57			
10	157	26	56			
11	153	26	56			
12	137	26	58			

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S	
A	165.2	10.1	10.2	6.3	
B	159.9	13.2	0.4	8.1	

Comments: Night run

Table B-4. Field Atmospheric Conditions

Site Youngstown, OH
Date 9-15-76
Exp. No. Y-1c

Flow Rates:
A 43.5 cfm
B 43.9 cfm

Filters:
A ADL
B OAST

Sample Time 11.75 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	168					
2	138					
3	217					
4	160					
5	159					
6	149					
7	109					
8	101					
9	106					
10	114					
11	104					
12	91					

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	175.4	11.39	<0.2	8.29
B	170.0	11.73	<0.2	7.76

Comments:

Table B-5. Field Atmospheric Conditions

Site Youngstown, OH
Date 9-15/16-76
Exp. No. Y-1d

Flow Rates:
A 43.8 cfm
B 44.3 cfm

Filters:
A ADL
B QAST

Sample Time 11.87 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	67	20	72			
2	62	20	74			
3	48	20	82			
4	25	19	82			
5	<15	20	81			
6	<15	20	78			
7	<15	20	79			
8	<15	19	85			
9	<15	18	90			
10	35	18	91			
11	48	19	91			
12	50	19	91			

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	51.5	2.1	-0.2	2.5
B	47.9	3.1	1.5	2.8

Comments: Night run, some rain

Table B-6. Field Atmospheric Conditions

Site Youngstown, OH
Date 9-16-76
Exp. No. Y-1a

Flow Rates:
A 44.1 cfm
B 44.3 cfm

Filters:
A ADL
B MSA

Sample Time 7.30 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	33	17	92	5		
2	<15	17	95			
3	<15	17	96			
4	<15	17	96			
5	<15	17	95			
6	<15	17	96			
7	<15	17	97			
8						
9						
10						
11						
12						

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	23.9	0.35	<0.4	1.3
B	30.4	0.22	<0.4	3.1

Comments: Rain

Table B-7. Field Atmospheric Conditions

Site Youngstown, OH
Date 9-16/17/76
Exp. No. Y-1f

Flow Rates:
A 43.9 cfm
B 43.8 cfm

Filters:
A ADL
B MSA

Sample Time 12.00 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	18	17	98	10		
2	34	17	98	30		
3	46	17	96			
4	51	17	94			
5	55	17	97			
6	59	17	98			
7	66	17	99			
8	68	17	98			
9	72	17	98			
10	73	17	98			
11	77	17	97			
12	77	17	98	<10		

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	27.6	9.53	1.0	1.7
B	31.4	6.68	0.4	3.88

Comments: Night run -- Rain

Table B-8 Field Atmospheric Conditions

Site Youngstown, OH
Date 9-17-76
Exp. No. Y-1g

Flow Rates:
A 44.6 cfm
B 44.3 cfm

Filters:
A ADL
B ADL + MnO_2

Sample Time 11.78 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	62	17	99	<10		
2	33	16	100	<10		
3	24	17	100			
4	39	17	99			
5	67	17	96			
6	34	17	97			
7	29	17	99			
8	27	17	98			
9	36	17	96			
10	40	18	94			
11	39	17	95			
12	44	16	98			

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	55.0	3.35	0.4	3.02
B	60.0	1.91	0.2	3.95

Comments: Rain

Table B-9. Field Atmospheric Conditions

Site Youngstown, OH
Date 9-18/19-76
Exp. No. Y-1h

Flow Rates:
A 44.5 cfm
B 44.7 cfm

Filters:
A ADL
B ADL + MnO_2

Sample Time 11.92 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	102	18	62	20		
2	84	17	70			
3	79	15	82			
4	76	16	81			
5	66	15	87			
6	63	16	86			
7	83	16	84			
8	82	16	85			
9	80	16	89			
10	87	16	93			
11	79	15	97			
12	93	16	97	5		

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	188.7	5.54	1.44	5.77
B	175.7	7.50	-0.2	7.40

Comments: Night run

Table B-10 Field Atmospheric Conditions

Site Youngstown, OH
Date 9-18-76
Exp. No. Y-11

Flow Rates:
A 43.9 cfm
B 43.8 cfm

Filters:
A ADL
B ADL + Fe_2O_3

Sample Time 11.50 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO_x, ppb	NO_2, ppb
1	70	15	91			
2	66	15	90			
3	77	17	86			
4	89	19	84			
5		20	82			
6	87	21	66			
7	98	23	59			
8	99	26	39			
9	118	25	38			
10	121	24	37			
11	129	22	41			
12	120	20	50	20		

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	331.0	6.75	0.5	6.41
B	273.7	5.48	-0.2	6.78

Comments: Wind shift -- directly from dirtiest stack

Table B-11. Field Atmospheric Conditions

Site Columbus, OH
Date
Exp. No. FC-1

Flow Rates:
A 44.6 cfm
B 43.8 cfm

Filters:
AMSA-1106-BH
BADL

Sample time 12 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_2, ppb
1	35.0	14.0	78.8			
2	44.6	13.4	83.8			
3	46.2	13.0	85.0			
4	45.5	12.6	86.6			
5	48.7	12.4	87.8			
6	42.5	12.7	85.4			
7	40.4	12.1	88.8			
8	34.9	12.3	87.5			
9	26.6	12.3	90.8			
10	18.3	12.7	87.7			
11	(9.0)	13.2	87.2			
12	(2.2	14.8	79.4			

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	56.4	0.572	0.55	3.74
B	54.9	0.661	0.11	1.46

Comments: Night run, no NO_2 or O_3 measured

Table B-12 Field Atmospheric Conditions

Site Columbus OH
Date
Exp. No. FC-2

Flow Rates:
A 43.5 cfm
B 43.3 cfm

Filters:
A MSA
B ADL

Sample Time 12 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	39.6	19.1	63.9			
2	62.7	21.0	61.2			
3	54.1	22.3	59.4			
4	41.8	25.1	48.8			
5	47.9	24.5	49.8			
6	54.5	24.1	51.6			
7	64.8	24.0	48.6			
8	69.8	23.6	42.6			
9	74.1	22.5	48.1			
10	75.1	21.6	52.1			
11	73.9	20.3	56.3			
12	73.9	19.1	60.5			

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	87.1	3.52	0.56	5.07
B	83.0	3.50	1.13	3.96

Comments: Day run, no NO_x or O_3 measured

Table B-13. Field Atmospheric Conditions

Site Pym-tuning
Date 9-19/20-76
Exp. No. P-1a

Flow Rates:
A 44.5 cfm
B 44.5 cfm

Filters:
A ADL
B Gelman A

Sample Time 12.42 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	63	15	98	28		
2	76	13	99			
3	94	12	99			
4	109	12	99			
5	97	12	97			
6	85	12	98			
7	80	12	98			
8	74	13	100			
9	72	14	100			
10	71	15	100			
11	67	15	100			
12	60	16	99	30		

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	56.4	5.42	0.4	6.71
B	45.9	5.14	-0.4	6.71

Comments: Light rain, NO_x instrument not working

Table B-14. Field Atmospheric Conditions

Site Pymatuning
Date 9/20/76
Exp. No. P1b

Flow Rates:
A 44.3 cfm
B 44.9 cfm

Filters:
A ADL
B Gelman A

Sample Time 11.45 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	42	14	98	15		
2	54	14	100	12		
3	63	15	100	33		
4	71	15	100	38		
5	73	15	97	43		
6	75	16	95	37		
7	72	17	91	36		
8	70	16	95	28		
9	76	16	91	29		
10	80	16	92	28		
11	90	15	95	8		
12	100	15	100	25		

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	41.8	4.75	2.4	4.64
B	39.2	5.64	1.8	7.44

Comments: Light rain

Table B-15. Field Atmospheric Conditions

Site Pymatuning
Date 9-20/21-76
Exp. No. P-1c

Flow Rates:
A 44.8 cfm
B 44.8 cfm

Filters:
A ADL
B OASY

Sample Time 11.75 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	75	14	100	25		
2	87	13	100	10		
3	96	13	100			
4	103	13	100			
5	108	13	100			
6	107	12	100			
7	96	12	100			
8	88	12	100	10		
9	83	12	100	8		
10	79	12	100	9		
11	74	11	99	14		
12	69	9	100	10		

Filter Loading, $\mu g/m^3$

	Particulate	$SO_4^=$	$SO_3^=$	S	
A	11.8	0.1	0.45	1.13	
B	11.6	0.88	1.0	0.9	

Comments:

Table B-16. Field Atmospheric Conditions

Site Pymatuning
Date 9-21-76
Exp. No. P-1d

Flow Rates:
A 44.9 cfm
B 44.9 cfm

Filters:
A ADL
B QAST

Sample Time 11.62 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	54	9	100	20		
2	58	12	93	18		
3	65	14	71	21		
4	68	15	61	27		
5	55	15	60	22		
6	79	17	45			125
7	105	16	48			125
8	105	15	52	33		95
9	92	12	71	12		65
10	92	9	100	-5		60
11	99			13		70
12	98	8	96	23		75

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	13.9	0.33	1.31	0.68
B	11.9	0.20	0.48	0.80

Comments: Rain, NO_x instrument partly repaired

Table B-17. Field Atmospheric Conditions

Site Pymatuning
Date 9-21/22-76
Exp. No. P-1e

Flow Rates:
A 44.5 cfm
B 44.6 cfm

Filters:
A ADL
B MSA

Sample Time 11.77 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	87	6	89	20		40
2	89	6	91			43
3	82	6	94			78
4	89	6	94			100
5	91	6	96			120
6	94	6	93			130
7	96	6	96			130
8	97	6	96			135
9	97	6	94			130
10	96	7	87			120
11	89	6	96			113
12	87	6	96	14		90

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	6.1	-0.3	1.5	0.34
B	9.3	1.88	1.0	4.4

Comments:

Table B-18. Field Atmospheric Conditions

Site Pymatuning
Date 9-22-76
Exp. No. P-1F

Flow Rates:
A 14.6 cfm
B 44.7 cfm

Filters:
A ADL
B MSA

Sample Time 11.75 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	75	5	95	15	35	70
2	83	6	86			58
3	90	8	78			70
4	86	10	65	20	45	66
5	20	11	58			70
6	28	11	53			97
7	38	12	53			80
8	40	12	53	30	45	65
9	33	13	50			47
10	42	13	50			53
11	53	12	54			70
12	59	9	80	15	45	95

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	15.4	0.0	0.45	0.56
B	18.5	4.69	1.90	5.08

Comments:

Table B-19. Field Atmospheric Conditions

Site Pymatuning
Date 9-22/23-76
Exp. No. P-1g

Flow Rates:
A 44.2 cfm
B 44.2 cfm

Filters:
A ADL
B ADL + MnO_2

Sample Time 12.10 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	16	6	100	15	30	30
2	40	5	100			40
3	46	4	100			55
4	47	5				50
5	47	5				63
6	45	6				63
7	39	7				60
8	50	8	100			63
9		9				68
10		9				70
11		9				70
12		8	99		40	70

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	28.2	1.09	0.4	1.76
B	29.1	1.86	0.4	2.20

Comments: Rain

Table B-20. Field Atmospheric Conditions

Site Pymatuning Flow Rates: Filters:
Date 9-23-76 A 44.7 cfm A ADL
Exp. No. P-ih B 44.7 cfm B ADL + MnO_2

Sample Time 11.50 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1		8	96	20	40	55
2		9	97			45
3	<15	10	97			53
4	<15	11	98	20	30	70
5	<15	12	90			75
6	16	12	90	25	40	75
7	26	12	89			90
8	40	13	80			67
9	48	12	93	35	45	65
10	37	13	93			75
11	40	12	96			65
12	40	11	100	30	35	65

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S	
A	30.3	1.02	1.49	1.60	
B	30.9	2.05	0.45	2.29	

Comments: Rain

Table B-21. Field Atmospheric Conditions

Site Pymatuning
Date 9-23/24-76
Exp. No. P-11

Flow Rates:
A 45.0 cfm
B 44.7 cfm

Filters:
A ADL
B ADL + Fe_2O_3

Sample Time 11.77 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1		8	100	30	30	40
2	<15	5	100			65
3	18	5	100			75
4	18	4	100			80
5	17	3	100			60
6	<15	2	100			40
7		1	100			48
8		1	100			50
9		1	100			--
10		0	100			--
11		0	100			--
12		0	97			--

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	12.1	<0.1	1.44	0.33
B	12.3	<0.2	1.01	0.57

Comments: Pens stopped on NO_x, O_3

Table B-21. Field Atmospheric Conditions

Site Pymatuning
Date 9-24-76
Exp. No. P-11

Flow Rates:
A 44.3 cfm
B 44.5 cfm

Filters:
A ADL
B ADL + Fe_2O_3

Sample Time 11.75 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1		2	96	0	35	35
2		7	90			33
3		10	77			25
4		11	57	20	35	40
5		14	51			21
6	<15	15	48			28
7	44	14	48			44
8	53	13	54	30	40	40
9	29	13	57			30
10	17	12	51			25
11		13	53			33
12		8	89		30	48

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	5.5	-0.35	0.45	0.0
B	4.8	-0.35	0.45	0.11

Comments:

Table B-22. Field Atmospheric Conditions

Site Pymatuning
Date 9-24/25-76
Exp. No. F-20

Flow Rates:
A 44.7 cfm
B 44.6 cfm

Filters:
A MSA
B MSA

Sample Time 11.50 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	97	6	86		30	53
2	107	3	100			50
3	107	2	100			35
4	111	2	100			35
5	106	1	100			37
6	104	0	100			44
7	107	0	100			51
8	114	0	[illegible]			42
9	114	0	[illegible]			39
10	111	0	100			36
11	117	-1	100			41
12	109	-1	100		40	40

Filter Loading, ug/m^3

	Particulate	SO_4	SO_3	S
A	17.1	-1.1	-0.5	2.86
B	14.6	0	1.0	2.06

Comments: SO_2 spike
Ambient SO_2 ~30 ppb

Table B-23. Field Atmospheric Conditions

Site Pymatuning
Date 9-25-76
Exp. No. P-2b

Flow Rates:
A 44.1 cfm
B 43.8 cfm

Filters:
A Gelman A
B Gelman

Sample Time 11.77 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	105	1	100		40	40
2		6	95			33
3		13	61			43
4	152	16	57	30	40	62
5	154	18	45			57
6	154	17	51			76
7	147	17	53	40	45	97
8	149	17	46			100
9	154	17	52			103
10	161	16	68			115
11	143	13	84			115
12	127	11	97		35	100

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	36.0	4.00	1.93	4.08
B	33.3	2.89	2.40	3.65

Comments: SO_2 spike
Ambient SO_2 ~30 ppb

Table B-24. Field Atmospheric Conditions

Site Pymatuning
Date 9-25/26-79
Exp. No. P-49

Flow Rates:
A 44.3 cfm
B 44.3 cfm

Filters:
A QAST
B QAST

Sample Time 11.80 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	137	9	100		40	60
2	134	8	100			70
3	139	8	100			70
4	140	9	100			70
5	138	9	100			70
6	133	9	100			88
7	140	8	100			88
8	145	8	239			80
9	151	8	100			75
10	151	8	100			65
11	154	9	100			55
12	153	9	100		30	55

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S	
A	14.2	2.11	2.16	2.70	
B	10.7	1.44	2.16	1.80	

Comments: SO_2 spike
Light rain
Ambient SO_2 ~60 ppb

Table B-25. Field Atmospheric Conditions

Site Pymatuning
Date 9-26-76
Exp. No P-2d

Flow Rates:
A 44.3 cfm
B 44.5 cfm

Filters:
A ADL
B ADL

Sample Time 11.78 hr

Hourly Averages

Hour	SO_2, ppb	T, °C	RH, %	O_3, ppb	NO, ppb	NO_x, ppb
1	125	10	98	~10	30	34
2	132	11	96			44
3	142	12	95			41
4	147	12	98			30
5	141	12	97	~10		49
6	150	13	99			53
7	141	13	100			72
8	141	14	100	~10	70	106
9	134	14	100			89
10	137	14	100			75
11	142	14	100			89
12	141	13	100	25	60	98

Filter Loading, $\mu g/m^3$

	Particulate	SO_4	SO_3	S
A	34.1	2.24	1.92	1.16
B	33.8	2.35	1.91	1.71

Comments: SO_2 spike
Rain
Ambient SO_2 ~60 ppb

APPENDIX C

LOS ANGELES FIELD SAMPLING DATA

As part of a cooperative effort between this work and that being conducted under Contract Nos. 68-02-2439 and 68-02-2213, additional sulfate field sampling data was collected in the Los Angeles area. In that program, approximately 250 filter samples were collected using various types of filters at three different sampling sites. Inasmuch as the data from the Los Angeles work is dedicated primarily for application on the above programs, analysis of that data has not yet been completed. However, sulfate data for one site at Upland, California (ca. 30 miles east of Los Angeles) is presented in Table C-1. Corresponding hourly average readings for temperature, relative humidity, and SO_2 are shown in Tables C-2-C-6.

The comparatively small differences between the responses of the Gelman AA and QAST filters shown in Table C-1 are due primarily to two factors:

(1) The sample volumes used in the Los Angeles work were of the order of 5.6 m^3/cm^2 which is somewhat higher than that employed in normal hi-vol sampling. As noted on page 27, the sulfate error due to SO_2 absorption is inversely proportional to the flow per unit area.

(2) SO_2 levels in the Los Angeles area are generally much lower than those found in the Youngstown study, thus further minimizing the contribution of SO_2 sorption to sulfate error.

In general, these small differences and the fact that ambient conditions were relatively constant make it difficult to attempt any detailed correlation of measured sulfate levels with values estimated from Equation 9. However, it can be seen from Table C-1 that the average difference in filter response for either sulfate or total sulfur compares well with the range calculated from Equation 9.

TABLE C-1. LOS ANGELES SAMPLING DATA

Date	Filter	Run No.	$SO_4^=$ $\mu g/m^3$	$SO_3^=$ $\mu g/m^3$	S $\mu g/m^3$
10/18	Gelman AA	LA-1	31.5	1.0	11.5
	OAST	LA-1	36.1	-0.5	12.7
10/19	Gelman AA	LA-2	33.3	0	11.8
	OAST	LA-2	30.5	0.6	11.3
10/20	Gelman AA	LA-3	18.0	0.6	7.2
	OAST	LA-3	9.2	0	3.8
10/21	Gelman AA	LA-5	18.3	0.6	6.7
	OAST	LA-5	18.3	1.4	6.2
10/22	Gelman AA	LA-6	12.0	0.6	4.9
	OAST	LA-6	11.8	1.2	4.3

ΔSO_4 = 1.5±5 $\mu g/m^3$

ΔS = 2.1±½ $\mu g/m^3$ (expressed as sulfate)

$\Delta \overline{SO_4}$ (Equation 9) = 1.2±0.1 $\mu g/m^3$

TABLE C-2. LOS ANGELES AMBIENT CONDITIONS (HOURLY AVERAGES)

Date	Hour, PST	T, °C	RH, %	SO_2, ppb
10/18	9-10	17.1	87.0	-(a)
	10-11	18.0	81.8	-
	11-12	19.2	75.5	-
	12-1	20.6	68.0	-
	1-2	22.4	61.0	-
	2-3	22.8	57.3	-
	3-4	22.0	58.0	-
	4-5	20.3	61.2	-
	5-6	18.0	73.8	-

(a) Instrument not working.

TABLE C-3. LOS ANGELES AMBIENT CONDITIONS (HOURLY AVERAGES)

Date	Hour, PST	T, °C	RH, %	SO_2, ppb
10/19	9-10	19.8	74.2	-(a)
	10-11	23.4	61.6	-
	11-12	26.5	47.6	-
	12-1	26.3	46.3	-
	1-2	25.2	47.6	-
	2-3	25.6	43.6	-
	3-4	24.2	48.0	-
	4-5	22.4	55.1	48.2

(a) Instrument not working.

TABLE C-4. LOS ANGELES AMBIENT CONDITIONS (HOURLY AVERAGES)

Date	Hour, PST	T, °C	RH, %	SO_2, ppb
10/20	9-10	20.1	63.3	74.7
	10-11	23.7	49.5	79.1
	11-12	25.3	42.5	60.5
	12-1	24.5	44.6	57.4
	1-2	22.5	56.4	49.5
	2-3	24.6	42.3	51.7
	3-4	25.8	34.2	51.0
	4-5	24.4	37.1	50.0

TABLE C-5. LOS ANGELES AMBIENT CONDITIONS (HOURLY AVERAGES)

Date	Hour, PST	T, °C	RH, %	SO_2, ppb
10/21	9-10	18.9	87.8	42.2
	10-11	20.2	81.3	44.4
	11-12	22.4	69.4	45.3
	12-1	24.3	59.7	47.3
	1-2	24.8	57.1	49.4
	2-3	24.3	59.2	55.5
	3-4	22.5	63.3	53.6
	4-5	20.4	68.2	51.0

TABLE C-6. LOS ANGELES AMBIENT CONDITIONS (HOURLY AVERAGES)

Date	Hour, PST	T, °C	RH, %	SO_2, ppb
10/22	9-10	18.8	82.0	52.5
	10-11	19.5	78.2	52.6
	11-12	20.8	70.6	52.5
	12-1	22.3	66.9	53.6
	1-2	20.5	68.2	53.4
	2-3	19.7	65.0	50.5
	3-4	17.5	70.9	48.8
	4-5	16.4	75.9	53.6

APPENDIX D

FILTER IDENTIFICATIONS

TABLE D-1. FILTER IDENTIFICATIONS

Filter	Chemical Type	Manufacturer
MSA-1106-BH	glass fiber	Mine Safety Appliance Co.
Gelman AE	glass fiber	Gelman Instrument Co.
Gelman AA[a]	glass fiber	Gelman Instrument Co.
Spectrograde	treated glass fiber	Gelman Instrument Co.
ADL[b]	quartz	Arthur D. Little, Inc.
QAST	quartz	Pallflex Products Co.
E 70/2075-W	glass fiber-EVA binder	Pallflex Products Co.
Mitex	Teflon	Millipore Corp.
Fluoropore	Teflon/polyethylene	Millipore Corp.
Celotate	cellulose acetate	Millipore Corp.
Duralon	nylon	Millipore Corp.
Polyimide	polyimide	Gelman Instrument Co.

(a) Obtained from R. Thompson, EPA.

(b) Similar material recently made available through Gelman Instrument Co.